EE/CA and RI/FS Support Sampling Plan

Sauget Area 1

Sauget and Cahokia, Illinois

Volume 2 - Appendix B

Soil, Groundwater, Surface Water, Sediment and Air FSP, QAPP and HASP

April 9, 1999

Submitted To:

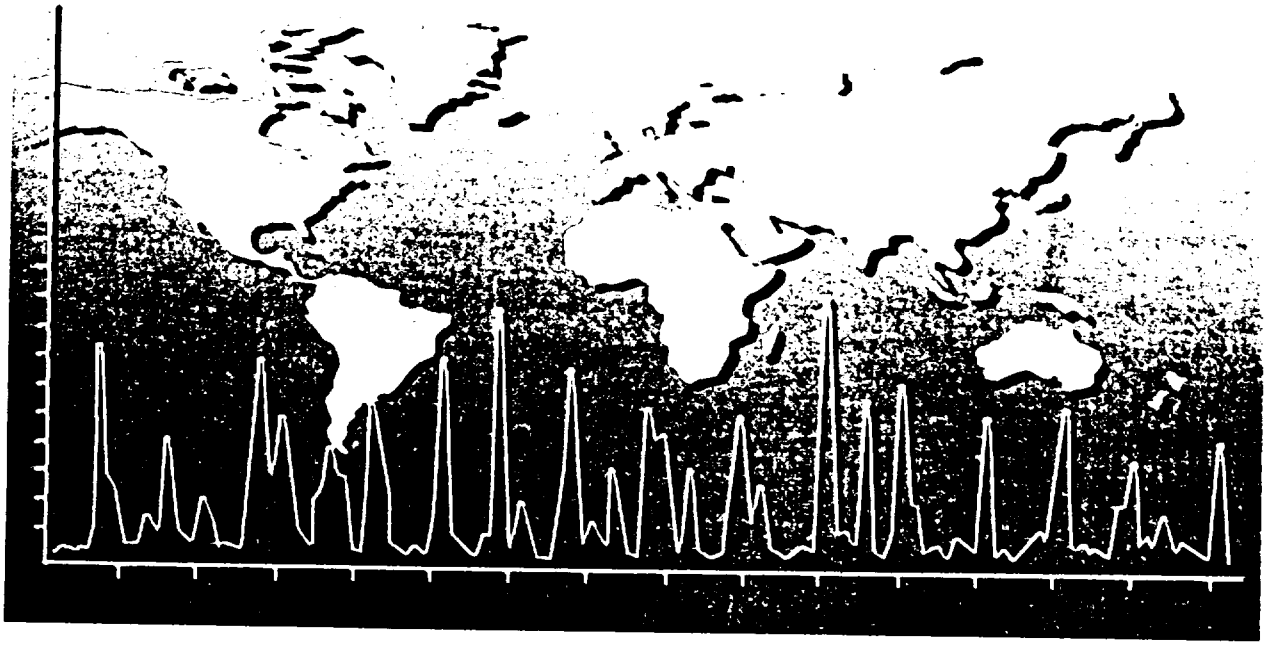
U.S. Environmental Protection Agency
Chicago, Illinois

Submitted **By:**

Solutia Inc.

Appendix B

Laboratory standard operating procedures and quality assurance manual for Triangle Laboratories, Inc.



Quality Assurance
Triangle Laboratories, Inc.

YOUR ANALYTICAL SOURCE

1998

MISSION STATEMENT

Triangle Laboratories is in the business of applying scientific knowledge and measurement to the solution of health, environmental and other issues confronting society.

Beliefs

We believe that we must excel in relationships with our customers, our employees, and our investors while establishing leadership in our technology and operations management.

We believe that in all things and at all times our behavior must follow the highest ethical standards. This includes commitments made to customers, suppliers, employees, investors, and to one another.

We believe that to our customers, we must be the laboratory of choice. Our marketing program will always honestly inform. We will set the quality and timeliness standards in our markets. We will structure our company so that we have the flexibility and versatility required to be responsive to customer's needs. We will work until the customer is satisfied.

We believe that for our employees, we must be the employer of choice. Through the application of high ethical standards, maintenance of efficient operations and a respect for diversity, we will provide a work environment that enriches and builds people while giving them an opportunity to excel and enjoy the dignity, pride, and material rewards of being part of a winning team.

We believe that for our investors, we must commit to the development of long term value in their investment. This will be accomplished by taking those risks that have an appropriate probability of reward, controlling expenses to maintain high profitability and aggressively seeking opportunities to achieve growth through expansion of existing business and developing new business opportunities.

We commit ourselves to conducting research and development so that we are always a leader in technology, to apply the knowledge gained to maintain efficient operations and to service our customers needs in a timely manner while providing a reasonable profit for our investors.

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Section 1

INTRODUCTION

This manual is a description of the quality assurance program employed at Triangle Laboratories, Inc., referred to hereafter as Triangle Labs or TLI. It is intended to provide employees, accrediting agencies, and clients with the information needed to understand how an effective quality assurance system is maintained at Triangle Labs. The QA Manual is divided into fifteen sections and several appendices. The first three sections pertain to the manual itself. Sections 4 - 7 provide general descriptions of Triangle Labs, including its objectives, policies, facilities, organization, personnel, and services. The remaining sections describe specific quality assurance activities as practiced within different functions or work units. The order of sections 8 - 12 closely follows that of the production process at Triangle Labs. The appendices provide supplemental materials that support the descriptions in the QA Manual sections.

Written procedures for implementing the activities described in this manual are maintained as standard operating procedures (SOP's) and as department specific training procedures. The SOP's are made available to the operating staff through the widely distributed SOP Manuals. The training procedures are maintained by the department managers. The provisions of this manual are binding upon all laboratory personnel assigned responsibilities described herein. All laboratory personnel must adhere implicitly to the Standard Operating Procedures.

Section 2

AUTHORIZATION

The quality assurance system described in this Quality Assurance Manual has the absolute support of the management at Triangle Labs.

The provision of quality analytical services to our customers has given us an enviable reputation and has made us a leader in the industry. Assuring that we maintain this status in providing quality products to our customers is the responsibility of every member of the laboratory staff. It is hoped that everyone concerned will use this manual as a guide to quality improvement and to maintenance of our current standing as a quality-oriented laboratory.

Signature:	Date:
J. Ronald Hass President and Chief Executive Officer	11/17/97
Patty L. Ragsdale Quality Assurance Manager	11/17/97
Donald J. Harvan Vice-President	11/14/97
Phil Albro Technical Director	11/17/97

Section 3

MANAGEMENT OF THE QUALITY ASSURANCE MANUAL

The Quality Assurance Department is responsible for the publication and distribution of the Quality Assurance Manual. The manual is submitted to senior management for review and authorization annually. As major changes are implemented in the quality assurance system, the Quality Assurance Manual is revised and submitted to management for authorization. The assistance of laboratory management is essential for the publication of the QA Manual. Department specific information is supplied by the department supervisors for inclusion in the manual.

The authorization signatures found in Section 2 of the manual signify management review and approval of the Quality Assurance Manual. The authorization section must be kept current and reflect any organizational changes affecting the authorizing positions. The revision date for the authorization section must be the most recent of any section in the manual, indicating that all revisions have undergone management review.

Document control procedures are applied to the distribution of the Quality Assurance Manual. Controlled copies are serially numbered and are updated each time a section is revised. Controlled copies of the manual may be distributed to an individual or a department. Uncontrolled copies may be issued to persons or organizations outside of Triangle Labs. These copies are distinctly marked "uncontrolled" and are not subject to updates upon revision of the manual. A distribution list is maintained for all copies of the Quality Assurance Manual.

Upon revision, all text added or changed since the last issue of each section is marked with a vertical bar in the margin.

Section 4

OBJECTIVE AND POLICIES

Objective

The objective of the staff at Triangle Laboratories, Inc. is to provide products and services which satisy our clients' expectations and definitions of quality and which are legally defensible.

Policies

The management of Triangle Labs supports the following policies in order to achieve the objective and promote the overall quality assurance program:

- Standard operating procedures shall be implemented in order to determine client requirements and to clearly communicate these requirements within the laboratory.
- Organizational emphasis on quality improvement will take place through strong management commitment and leadership, employee empowerment and teamwork.
- A comprehensive quality control system shall be established and maintained in order to verify and assure continued precision and accuracy of analytical results.
- Adequate training on laboratory operations shall be available to all employees whose decisions may affect the quality of laboratory products.
- A comprehensive program of documentation shall be implemented to ensure maintenance of accountability and traceability throughout the analytical process.
- Measures shall be implemented to ensure that sample integrity is protected.
- Validation studies shall be performed for each analytical method, including extensive evaluations whenever major modifications have been implemented.

- The instrumentation, equipment, and materials used in the production process shall be controlled (i.e., purchased, verified, calibrated, maintained, monitored, and evaluated) to ensure that required standards are met.
- A comprehensive program for data reduction, validation, reporting, and archival shall be implemented.
- Preventive and corrective actions shall be taken to eliminate the causes of potential or actual nonconformance. Emphasis shall be placed on preventive measures.
- Measures shall be implemented in order to meet the requirements set forth by agencies from whom certifications and accreditations have been granted.

Section 5

LABORATORY DESCRIPTION

Triangle Laboratories, Inc.

The location, mailing address, and phone numbers for Triangle Laboratories, Inc. are:

Triangle Laboratories, Inc.
801 Capitola Drive
Durham, North Carolina 27713

P.O. Box 13485
Research Triangle Park, North Carolina 27709

(919) 544-5729
(919) 544-5491 (Facsimile)

Triangle Laboratories, Inc. is a privately held subchapter C Corporation registered and incorporated in the state of Delaware. Triangle Laboratories has been in business since 1984 and has established an unparalleled reputation for integrity and quality while undertaking the most challenging work in its industry. The company experienced rapid growth during the emergence of the environmental market. Recognizing the necessity of diversification even while the environmental business was in full swing, the company expanded internationally as well as moving into new markets. Triangle Laboratories currently serves two major market areas, environmental and pharmaceutical.

Facilities and Instrumentation

Triangle Laboratories, Inc. currently occupies more than 50,000 square feet. The facility is divided according to work function, including separate areas for sample receipt; sample, standard, and glassware preparation; sample and data storage; instrumentation; report generation, quality assurance; shipping; maintenance; and business/management offices.

Analytical instrumentation at Triangle Labs includes: high resolution gas chromatograph/high resolution mass spectrometers (HRGC/HRMS); high resolution gas chromatograph/low resolution mass spectrometers (HRGC/LRMS); high pressure liquid chromatograph/mass spectrometer/mass spectrometers (HPLC/MS/MS); high pressure liquid chromatograph (HPLC) with ultraviolet detector (UV); gas chromatographs (GC) with electron capture detectors (ECD) and flame ionization detectors(FID); AOX/TOX adsorption module and microcoulometric titration systems; ion chromatographs (IC); inductively coupled plasma atomic emission spectrophotometers (ICP) and atomic absorption spectrophotometers (AA).

Well maintained equipment is essential in assuring the timely delivery of complete, high quality analytical data to clients. This is facilitated through a program of regular maintenance for all equipment, equipment redundancy, an ample stock of spare parts, and an inventory of specialized test equipment to support rapid repair when unscheduled maintenance is required. Service technicians are available through contracts with local providers for most of the instruments. Procedures and schedules for preventive maintenance are available in several SOP's. All instrument maintenance, both preventative and corrective, is recorded in the dedicated maintenance logbook assigned to each instrument.

Environmental and Security Systems

Triangle Labs provides a secure environment for our employees, guests, clients, samples and analytical data.

Access

Standard procedures require that all exterior doors remain locked via keylock or combination lock unless manned. Visitors are required to sign the Visitor Log and must be accompanied by an employee of Triangle Labs.

The defined high security areas include all laboratories, data archives, computer system, data reduction offices, and quality assurance offices. Entry into these areas of the building are controlled by combination locks on the internal and external entry doors. Visitors must be accompanied by an employee of Triangle Labs at all times inside the high security area.

Several rules apply to protecting the combination lock codes. The combinations are changed periodically. New combinations are supplied to the active employees only by the employee's supervisor or the facility manager. When accompanied by visitors, employees obscure the punch lock combination from view.

Security

All doors are locked after hours and require a key for entry. The security alarm at Triangle Labs offers continuous monitoring for smoke, extreme fire related heat, cold room temperatures, motion, and door contacts. Panic buttons are located throughout the building which set off an audible alarm and call the central station when activated.

Archives

Limited access archive facilities are maintained that house all Triangle Labs copies of analytical reports, raw data, inactive logbooks, magnetic tapes and other data which facilitate traceability of analytical results. Materials housed in the archives are packaged to reduce potential damage from fire and water.

Chemical Storage and Disposal

All chemicals are stored in appropriate cabinets and are properly disposed of when necessary. All flammable solvents are kept in OSHA and NFPA approved cabinets. Acids are stored in OSHA approved acid cabinets. An authorized waste carrier is contracted to pick up lab waste monthly and dispose of it, usually by incineration, meeting all regulatory requirements. Post-analysis disposition of samples is dependent upon client requests. Remaining sample material may be returned to

the client, safely discarded, or archived for a specific period of time.

Environmental Control

The working and storage environments are maintained in a safe and appropriate manner. Heating, ventilation and air-conditioning systems satisfy the needs of personnel, equipment and supplies. Lighting, noise and other environmental factors are also considered and kept at appropriate levels. Safety measures which protect personnel and property from injury or illness include the following: fume hoods, fire extinguishers and blankets, alarm systems, safety training, protective clothing, emergency showers, eyewashes and spill control kits. Triangle Laboratories has a contract with Duke University which provides an occupational health program for all employees.

Accreditations, Certifications, Licenses and Registrations

Triangle Laboratories, Inc. has received approval from several state and national agencies. The American Association for Laboratory Accreditation has conferred accreditation upon Triangle Labs for technical competence in environmental testing. The laboratory has been validated by the United States Army Corps of Engineers, and while not currently under contract, Triangle Labs has performed organic analyses under the United States Environmental Protection Agency (USEPA) Contract Laboratory Program. TLI is registered under current Food and Drug Administration (FDA) regulations to engage in the testing of drugs; has received registration under the provisions of the Clinical Laboratory Improvement Amendments of 1988 (CLIA) to perform high complexity testing (dioxin and PCB's) of human samples; has been licensed, and has been provisionally certified by several USEPA regions to analyze drinking water samples for dioxin.

Section 6

ORGANIZATION AND PERSONNEL

Organization

Responsibility and Authority

At Triangle Laboratories, the management structure is best illustrated by referring to the Organizational Chart in Appendix 1A. Responsibilities and authority of key personnel found on the charts will be summarized later in this section. Brief resumes of key Triangle Labs personnel may be found in the company's Statement of Qualifications.

Verification Resources and Personnel

Verification activities include inspection and monitoring of process and product quality and auditing of the quality system, processes and products. Provision is made for personnel to be trained and have responsibility for these activities.

Production personnel, under the direct supervision of area managers, are responsible for the inspection and monitoring of in-process and final products. Audits of the quality system and products are performed by personnel independent of those having direct responsibility for the work being performed. Quality system audits are carried out by Quality Assurance Department personnel, while data audits (audits of the final product) are carried out by employees in both Client Services and Quality Assurance.

Effective verification activities are achieved by the provision of adequate resources to personnel. These resources include adequate training, time for verification activities, knowledge about requirements, documented procedures, access to quality records, and adequate supplies and equipment necessary to perform verification.

Management Representative for Quality Assurance

The Quality Assurance Manager reports directly to the President, functions independently of production, and has the authority to implement and maintain the quality system. The management of Triangle Labs presents a strong commitment towards the important role of quality assurance in its organization. The Quality Assurance Manager and other members of the Quality Assurance Department interact frequently with personnel at all levels throughout the organization.

Management Review

A formal management review of the quality system occurs annually. The purpose of this review is to ensure that the quality system remains effective, meets the quality objectives and policies stated in Section 4 of this manual, and satisfies the requirements of state, national, and international certifications held by Triangle Labs. Records of management reviews shall be maintained in the

Quality Assurance Department.

Personnel

Job Descriptions of Key Technical Personnel

While not all-inclusive of assigned duties, the following are brief descriptions of the chief technical personnel at Triangle Labs.

President/Chief Executive Officer: management of administrative, business, quality assurance, personnel and production activities, through direct supervision of the Production Management Team, the Quality Assurance Manager; and the Technical Director, minimum qualifications - education: Ph.D. Chemistry, experience: 10 years analytical chemistry.

Quality Assurance Manager: coordination and management of the Quality Assurance Department; reports directly to the President; responsible for overseeing all quality aspects of the laboratory; specific elements to be maintained are: the Standard Operating Procedures, Quality Assurance Manual; coordination of internal and external audits. performance samples and laboratory certification data; minimum qualifications - education: B.S. Chemistry or equivalent, experience: 5 years in scientific field.

Production Management Team: comprised of the three Production Area Managers. The team functions as a single entity which is responsible for developing production plans to meet commitments made to clients, identifying and resolving issues which impede success, and promptly reporting to the president any issues which cannot be resolved with available resources.

Production Area Managers: management of a defined production area, instrumentation, reporting and/or sample preparation; minimum qualifications - education: B.S. Physical Science, experience: 5 years general analytical chemistry, 2 years supervisory.

Recruitment Policy

The Personnel Department of Triangle Labs uses several methods of recruitment. Current employees are offered the earliest opportunity to apply for openings within the facility by posting available positions on the bulletin boards one week before outside sources are considered for candidates. Then, announcements are made in local newspapers, placement agencies (temporary and permanent), colleges and the Employment Security Commission offices. The recruitment process consists of collecting applications and resumes, distributing them to the appropriate supervisors, scheduling interviews as requested by supervisors and having candidates meet with relevant staff and a representative from the Personnel Department. The references of promising candidates are investigated prior to making job offers.

Training

Training is provided for new employees and as continuing education for veteran employees, both at the Triangle Labs facility and off-site.

On-Site Training: Training goes on at different levels throughout the facilities. Numerous manuals, texts, videos, SOP's, journals, analytical protocols and in-house instructors are available to trainees. On-the-job training related directly to the position is done by area managers or other qualified staff. Typically, a trainee goes through a stepwise method to learn procedures pertaining to such areas as analytical methodology, report generation or quality assurance activities: he is given an SOP to read, he observes the trainer performing the procedure, he assists the trainer in performing the procedure several times, he performs the procedure without assistance but with the trainer's frequent inspection of his work, and finally, he may perform the procedure without supervision. The Quality Assurance Manual is available to all employees whose activities have a direct impact on product quality. Cross training, supervisory training and other related training takes place on a scheduled basis and is documented for training files.

Off-Site Training: This type of training takes place on an as-needed basis. Recommendations and suggestions about promising educational programs come from all levels of staff. Completed studies are documented and updated regularly in the training files. Courses may be taken at local colleges and universities. Workshops and seminars are often made available by instrument manufacturers, software companies and national associations specializing in analytical chemistry or laboratory quality assurance.

Training Records Maintenance

Résumés, education and experience records, job descriptions and training records are maintained by the personnel department: Résumés are put in a uniform format upon hire. These résumés are updated on an annual basis or as needed. Additional education and experience is updated with the résumés. There is a job description for each position existing within the company. Active training records are kept on file in the work areas. Employees are responsible for maintaining their own training records. These training files contain records for any pertinent on- or off-site educational experiences, orientation records, SOP competence records or self help courses, such as "Smoke Stoppers" or Stress Management.

Safety and Health Policies

All personnel undertake a one day orientation upon initial employment and on-the-job intensive training concerning health and safety issues. Triangle Labs complies with the OSHA requirement that safety and health training takes place on an annual basis, with a careful introduction to new principles. We have contracted with Duke University Medical Center Occupational Health Services to provide us with recommendations for the improvement of the safety and health practices at Triangle Labs and periodic medical examinations for all employees. Triangle Labs' policy with respect to health and safety issues is presented in detail in several documents, with which employees are provided.

Section 7

ANALYTICAL SERVICES

Triangle Labs has assembled an international staff of unparalleled expertise in analytical sciences with particular specialization in mass spectrometry and the analysis of complex biological matrices. The skills of the staff are routinely applied to environmental samples, including of air, water, solid and tissue matrices, and to biological samples associated with studies supporting the research efforts of the pharmaceutical industry.

Pharmaceutical Services

Triangle Labs serves the research pharmaceutical industry by providing analytical results for drugs of interest in a variety of biomatrices. This work is typically associated with pharmacokinetic Phase 1 through Phase IV studies for reporting to the Food and Drug Administration (FDA).

GC/MS and LC/MS/MS methods are typically employed for these analyses. High resolution mass spectrometers and alternate ionization methods are frequently utilized to achieve low detection limits. The staff is also experienced in assays, both GC and LC based, for chiral compounds.

Environmental Services

Triangle Labs provides environmental analytical services which include the preparation and analysis of a wide variety of sample matrices for such analytical categories as:

Volatile and Semivolatile Organic Compounds, including Polychlorinated Biphenyls, by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry

Pesticides and Herbicides by High Resolution Gas Chromatography

Polychlorinated Dibenzo-*p*-Dioxins, Polychloro-dibenzofurans, Polychlorinated Biphenyls, and Polynuclear Aromatic Hydrocarbons by High Resolution Gas Chromatography/ High Resolution Mass Spectrometry

Polychlorinated Dibenzo-*p*-Dioxins and Polychloro-dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry

Adsorbable Organic Halides and Total Organic Halides by Adsorption and Microcoulometric Titration

Inorganics by Ion Chromatography, Atomic Absorption Spectrophotometry, and

Inductively Coupled Plasma-Atomic Emission Spectrophotometry

Triangle Labs is experienced in the analysis of many matrices, including air, aqueous, plant and animal tissues, soils, and other solids. Air matrices currently analyzed include Modified Method 5 (MM5) samples and Volatile Organic Sampling Trains (VOST). Several auxiliary services are also offered, such as the provision and preparation of sampling containers (e.g., XAD traps, VOST tubes, and bottles).

Analytical Methodology and Target Compounds

Triangle Labs utilizes a variety of published and in-house analytical methods. In some cases minor modifications of methodology may be employed. Such modifications are validated prior to implementation in the laboratory. Target Compound Lists (TCL's) are chosen from the analytical methods. Published methodology utilized for each category of analytical services is listed below:

Volatile Organic Compounds (VOA) - Methods 8240, 8260 and 1624

Semivolatile Organic Compounds (SVOA) - Methods 8270

Pesticides - Methods 8081

Polychlorinated Biphenyls (PCB's) - Modified Method 680 and 8081

Polychlorinated Dibenzo-*p*-Dioxins (PCDD's) and Polychlorodibenzofurans (PCDF's) - Methods 8290, 23, 1613, 8280, 613 and NCASI 551

Adsorbable Organic Halides (AOX)/Total Organic Halides (TOX) - Methods DIN 38409, DIN 38414, EPA 9020, EPA 1650, PTS-RH: 012/90, SCAN-W 9:89, ISO/DIS 9562, and APHA 5320B

Inorganics - Ion Chromatography by Methods 7D, 26, 26A, 218.6, 300.0, and 9057; Trace Metals analyses by Methods 200.7, 6010, 7020, 7040, 7041, 7060, 7080, 7091, 7131, 7140, 7200, 7210, 7380, 7420, 7421, 7450, 7460, 7470, 7471, 7481, 7520, 7610, 7740, 7760, 7770, 7840, 7841, and 7870

Additional information about analytical services and methodology can be found elsewhere in this manual, and in the Analytical Services Guide. Selected analytical methods are summarized in Appendices 2 and 3 of this manual.

Triangle Labs has developed in-house methods for the analyses for Polynuclear Aromatic Hydrocarbons (PAH's) and Polychlorinated Biphenyls (PCB's by High Resolution Gas Chromatography/High Resolution Mass Spectrometry. These methods are proprietary and utilize state-of-the-art technologies.

Contract Review

For all analytical services to be provided by Triangle Labs, contract review is accomplished through the generation of a written quote or contract. Written quotes are utilized for short-term contracts, usually consisting of one analytical project. Written contracts are utilized for long-term contracts consisting of multiple analytical projects. Sales and Client Services personnel are responsible for implementing and documenting contract review. Client requirements, including special needs that are not normally provided by Triangle Labs, are defined and documented in the written quote or contract. Project scientists, who each have expertise in specific analytical services, are consulted to ensure special requirements can be met by the laboratory. If it is decided that the special requirements cannot be met, this is discussed with the client, and a counterproposal may be offered. Information about the capacity of the lab is made available to Sales and Client Services personnel on a regular basis. This practice allows the sales staff to make informed decisions regarding contracted delivery times.

Subcontracted Analyses

In dealing with any analyses that Triangle Labs cannot perform, there are established procedures for subcontracting. Depending on the nature of the client's requests for analyses, two courses of action may be followed. The client may be referred directly to another laboratory, if known; or work may be subcontracted by TLI to another laboratory. The latter usually takes place when Triangle Labs is able to perform part of the requested analyses. When the subcontracted analysis is one that Triangle Labs has been certified to perform, the subcontract lab must have a quality assurance system in place that is consistent with Triangle's system. Incoming samples which will be subcontracted are subjected to normal sample receipt procedures by the sample custodian. The samples are prepared and shipped to the subcontract laboratory. Results are received at Triangle Labs, a copy is sent to the client, and the original is archived. Triangle Labs invoices the client for the subcontracted work.

Section 8

LABORATORY MATERIALS—PURCHASING AND HANDLING

Purchasing, Receiving, Inspection, Inventory and Storage of Laboratory Materials

Practices utilized for the purchase, receipt, inspection, inventory, and storage of laboratory materials are described in several SOP's. A completed purchase requisition form provides a clear description of the product ordered. This includes, where applicable, a precise identification and reference to any specifications that must be met. Purchases are pre-approved by department heads. The purchasing department orders the material, from an approved supplier whenever possible. Upon receipt of the goods, receiving personnel examine them for damage before signing the bill of lading. Within two days, items and quantities in all shipments are compared with what was ordered and this information is communicated to purchasing and accounts payable. All stocked items are stored in the warehouse and a monthly inventory is performed. Non-stocked inventory is forwarded to the requisitioning person. Reagent materials are assigned expiration dates and placed on shelves so that the older materials will be used first.

Sample Container Cleaning, Storage, Preparation and Shipping

While Triangle Labs does not perform sampling, sampling kits may be provided upon client request. The vials, jars, and bottles contained in the kits are purchased and must be QC class, precleaned, with a certificate of analysis. The certificates of analysis are maintained by TLI. Since kits are assembled only upon clients' requests, no "ready for shipping" kits are stored. Precleaned glassware is stored in small quantities in house. Sampling materials, such as XAD traps, PUFs and VOST tubes, are also provided to or owned by the client. These are prepared, stored and handled as detailed in several SOP's.

All glass containers are wrapped in sheets of bubble wrap to prevent breakage. The containers are placed in plastic coolers with non-frozen ice packs and Chain-of-Custody forms, seals and labels enclosed in a ziplock bag. The kit is filled with additional packing material and sealed with tape for shipping.

Glassware Cleaning

All glassware used for the preparation of samples is cleaned as described in written standard operating procedures. These procedures include pre-rinses and soapy water washes. The pre-rinse may be solvent, water or acid solution depending on the analysis for which the glassware will be used. Basins and brushes are kept segregated so that cross contamination is minimized. Glassware used for high concentration analyses is kept segregated from glassware used for low concentration analyses, as is the glassware used for volatile, extractable organic compound and metals analyses. Glassware used for the analysis of extractable organic compounds, including dioxins and furans, is subjected to a solvent soak and rinses with several solvents. All clean

glassware is covered with aluminum foil and transferred to a proper storage location, taking care that the glassware is not intermixed with other types of glassware. In the Inorganic area, glassware is cleaned by a washing procedure that exceeds EPA guidelines. This glassware is washed with detergent, followed by acid soaks and multiple rinses with deionized water. The clean glassware is air-dried and stored in plastic bags.

Vendor Qualification

The process for qualification of vendors and the maintenance of an approved vendor list is detailed in the SOPs. Vendors subject to qualification are those who provide laboratory supplies, chemicals, and calibration services which directly impact on the quality of our product. Placement on the approved vendor list is based on the vendor's ability to meet one or more qualification factors which cover the purchased product. These factors include but are not limited to:

1. the vendor's quality system or product meets an applicable state, national, or international standard, based on third party certification
2. an acceptable quality assurance plan/survey, or on-site audit;
3. the vendor provides quality inspection documentation with each shipment or batch lot of product;
4. the vendor passes comprehensive inspections of three consecutive product shipments;

A vendor may be provisionally approved until qualification factor(s) are met, but in-house inspection of each batch lot of material is required. Previously approved vendors may be disqualified due to unacceptable performance.

Client Verification

When required by contract, the client or a representative may verify that purchased products conform to contract specifications. This verification may take place at the vendor's premises or at Triangle Labs. Client verification shall not be used as evidence of effective control of quality by the vendor and shall not absolve Triangle Labs of responsibility to provide an acceptable product.

Section 9

ANALYTICAL STANDARDS

During the analytical process, it is possible to obtain a variety of measurements. These include such measurements as volume, weight, concentration, pH, and temperature, to name just a few. The laboratory must implement practices that facilitate the traceability of these measurements to recognized standards of measurement.

Chemical Standards

The procurement, preparation, handling and storage of chemical standards is critical to the analytical process. It is through these chemical standards that reported analyte measurements in samples are traceable to reference values. Only the highest quality chemicals are used as reference materials at Triangle Labs. Whenever possible, standard solutions will be traceable to national standards, such as NIST, EPA or A2LA certified reference materials. Numerous written procedures describe the management of these analytical standards. These procedures are written to ensure consistency with the requirements of analytical methods and current certifications and accreditations.

Sources of Standards, Traceability and Verification

Triangle Laboratories purchases standards from approved suppliers of chemical standards. Occasionally, clients supply standards specifically for use in the preparation and analysis of their samples. Prior to using these standards, an agreement must be reached with the client about the handling and disposition of their standards. Information about these standards and any client requirements are recorded in the pertinent standards logbook. The chemist receiving a chemical standard shipment verifies that the information on the standard label is consistent with that on the supplier paperwork. Information about the standard is recorded in a standards logbook. Traceability of standard solutions is facilitated by the use of codes that unambiguously identify the supplier, materials and all derived preparations. Non-certified standard materials are verified against certified reference standards, when the latter are available. When certified reference standards are not available, second source verification is required.

Types of Standards

Analytical methodologies define a variety of standard solutions which are used by the laboratory. Included among them are: surrogate spikes, matrix spikes, internal standards, QC check standards, recovery standards, and calibration solutions. The composition and concentration of these solutions must conform to method specifications.

Standards are categorized at Triangle Labs according to the following definitions:

Primary Standard A neat standard received from a supplier.

Stock Standard	A solution of a primary standard at a high concentration, used to prepare secondary standards. These may be prepared in-house or received from a supplier.
Secondary Standard	A solution of one or more stock standards, with each analyte prepared at a selected concentration, to be used as a beginning mixture for preparation of calibration or spike solutions. These may be prepared in-house or received from a supplier.
Working Standard	A solution that will be used without dilution for instrument calibration or sample fortification. These may be prepared in-house from secondary standards, or purchased from a supplier.

Preparation of Standards

The preparation of any standard solution is performed by an experienced chemist (usually the Standards Preparation Chemist), and is documented in the appropriate standards logbook. New standard solutions are prepared as needed. The manner of preparation for a standard solution depends upon the required amount and concentration and its intended application. Several SOPs are utilized to assure the correct preparation and documentation of standard solutions.

All standards are assigned an expiration date. The supplier's assigned expiration date, if provided, is used for neat or primary standards. Otherwise, the expiration date is assigned based upon the supplier's date of preparation and the known stability of the analyte. (Some analytes are known to be highly volatile or to easily degrade or react.) When applicable, assigned expiration dates meet the requirements of analytical methods. A standard mixture is assigned an expiration date no later than that of the oldest components. The expiration date is only a guideline. Standards are removed from production prior to the assigned expiration date if deterioration is observed visually or analytically or if the integrity of the material can no longer be assured.

Analyte or standard components common to calibration solutions and associated sample fortification solutions may be of the same primary source or an independent source. Some methodologies require that primary standards of the same supplier batch or lot number be used for both. Certain spiked QC samples must be prepared from reference material that is independent of the associated calibration standards. New standards are prepared as necessary to meet these requirements.

Inventory and Storage

Documentation for all standards is carefully recorded in relevant standards logbooks and/or computer inventory system. The manner of storage for a

standard is determined by its type and expiration date or shelf life. All light sensitive standards are stored in amber vials or bottles. Environmental organic standards are kept in designated refrigerators/freezers. Pharmaceutical standards are stored according to the conditions specified in the associated protocol, validation report or stability report. Analytical standards are never stored together with samples or extracts.

Measurement Equipment

All equipment used for measurement and testing shall meet the specific requirements of pertinent analytical methods and applicable certification agencies. This includes small equipment, such as thermometers, analytical balances, pH meters, autopipetors, and volumetric glassware; as well as large equipment, such as gas chromatographs and mass spectrometers.

Written procedures for the operation of measurement equipment, large or small, shall contain the information described below, where applicable. In addition, Section 11 on "Instrumental Analysis" of this manual contains more specific information about the calibration and operation of large measurement equipment.

- What equipment the procedure is to be performed on, including equipment type
- How the equipment is to be calibrated and used for measurement
- What measurements are to be made
- Acceptance criteria for the calibrations, including the accuracy and precision required
- Corrective action for failed acceptance criteria, including assessment of previous calibration results
- Basis used for calibration (e.g., national standards of measurement, such as NIST, ASTM, and A2LA; participation in EPA and state performance evaluations; round-robin studies with other laboratories)
- Frequency at which the equipment will be calibrated, adjusted and checked
- What records will be maintained to document the calibration and use of measurement equipment
- How the calibration status for equipment is determined (e.g., a sticker or logbook entry)

- What environmental conditions are necessary before measurement equipment may be calibrated or used for measurement
- What adjustments to measurement equipment, including software, cannot be made due to possible invalidation of the calibration setting
- How measurement equipment is to be handled, preserved, and stored in order to maintain accuracy and fitness for use

Section 10

SAMPLE RECEIPT, HANDLING AND PREPARATION

Sample Receipt and Chain-of-Custody

The Sample Custodian or a designated assistant receives deliveries of all samples. A unique project number is assigned to each shipment of samples received from a client, and the first in-house records for the new project, including an internal Chain-of-Custody, are initiated. When samples are hand delivered by a customer, the individual's name is recorded on the internal Chain-of-Custody. The shipping containers, their contents, and accompanying client documentation are examined by the Sample Custodian. Information about the presence and condition of custody seals and the state of preservation of the samples is noted on the internal Chain-of-Custody. Any discrepancies in documentation or problems with sample condition are also noted and brought to the attention of the client, who may provide clarification or further instructions. The Sample Custodian assigns an internal sample ID to each sample, which is labelled on the sample container. The following information pertinent to each sample is recorded on the internal Chain-of-Custody: internal sample ID, client sample ID, sample matrix and storage location. The original internal Chain-of-Custody is placed in storage with the samples. The sample receipt and handling SOP's describe procedures for sample receipt and log-in, chain-of custody, along with those for handling sample shipment containers provided by clients.

Sample Preservation and Security

Samples are stored in a manner which ensures their integrity and security. Samples are stored at temperatures which meet specifications of the methodology and client. Depending on the nature of the sample and the requirements of the method, samples may be stored in a freezer at -70° C or at -20° C, in a refrigerator or cooler at 4° C, or in a cabinet at room temperature. Required preservation techniques may be found in Appendix 4 for most methods employed at Triangle Labs. Quality Assurance Project Plans (QAPP's) and protocols often give specific preservation requirements that must be observed. Addition of chemical preservative to sample containers normally takes place at the time of sample collection. Sample storage facilities at Triangle Labs are located within laboratory areas which are secured by locked doors. Internal chain-of-custody procedures and documentation pertaining to sample possession, removal from storage and transfer are outlined in written procedures. Care is taken to ensure that cross-contamination does not occur during sample storage. Temperatures of cold storage areas are monitored and recorded at least twice a day, and corrective action is taken as necessary. Walk-in coolers housing environmental samples and freezers used for pharmaceutical samples and standards are monitored electronically 24 hours a day. Further details about sample storage and preservation may be found in the sample receipt and handling SOP's.

Sample Preparation Procedures

Samples are prepared in a way that is method and matrix specific. Most environmental samples must be prepared within a method-specified time after sampling. These preparation holding times are complied with to the extent possible. Samples are occasionally received near or beyond the expiration of these holding times. For most methods employed at Triangle Labs, holding times may be found in Appendix 5. Applicable Quality Assurance Project Plans (QAPP's) and protocols must be consulted for project-specific holding time requirements. Many primary extracts require clean-up procedures before they may be injected into a GC or GC/MS analytical system. All sample preparation procedures employed at Triangle Labs are covered by appropriate SOP's.

Sample, Extract, and Digestate Archival and Disposal

The Sample Custodian and other authorized personnel are responsible for the archiving and disposal of raw samples, extracts, and digestates. Raw and prepared samples may not to be archived or disposed of until all of the designated analyses are complete and resultant analytical data are sent to clients. Samples in cold storage are retained there until at least 30 days after receipt. Archive samples are placed in boxes, labelled with the project numbers, and retained in a secured sample archive area for a specific length of time, prior to disposal. Written procedures describe routine archival and disposal practices. Clients are informed about these procedures and are given an opportunity to request exceptions to these routine practices. There is a storage fee for the retention of samples in cold storage or archive longer than the time established by routine practices.

Sample Return to the Client

When a client has requested the return of samples, the Sample Custodian prepares and ships the samples according to written procedures. Protection of the samples during delivery is ensured by the implementation of special packaging procedures. Packages are delivered by a commercial carrier whose procedures for protecting the samples are not within the control of Triangle Labs. Clients are informed that a commercial carrier will deliver their samples.

Sample Loss, Damage, or Unsuitability

It is possible for samples or sample containers to be lost, damaged or determined to be unsuitable, for whatever reason, after initial receipt at Triangle Labs. Whenever this happens, the event is recorded in the sample handling documentation by the observer. The problem is brought to the attention of a Project Scientist, who reports it to the client. Plans for disposition of the affected sample(s) or containers are agreed upon with the client, carried out, and recorded in the project records.

Section 11

INSTRUMENTATION AND EQUIPMENT

Instrumental analysis consists of setting up proper instrument operating conditions, executing acceptable calibrations and other instrument performance tests, analyzing prepared samples, and collecting data from the analyses. Instrumental analysis procedures, frequencies and acceptance criteria are described in several SOP's, the contents of which are derived from methods. A description of data collection and reduction at Triangle Labs is given in Section 12.

Instrument Operating Conditions

The published analytical methods normally define the optimum instrument operating conditions (e.g., temperature programs, column conditions, flow rates). Where applicable, these specifications will be followed, unless otherwise indicated for a project.

Calibration Procedures and Frequencies

Equipment used for inspection, measuring and testing must meet all specific requirements for proper measurement capability as identified in the pertinent analytical method and applicable certification agency. This includes small equipment and instruments as well as large analytical instruments such as gas chromatographs and mass spectrometers. Calibration procedures and frequencies specific to types of equipment are briefly described below.

The instrumental performance requirements of the published methods will be followed unless otherwise specified for a project. Other performance tests may also be executed to further demonstrate proper functioning of instrumentation.

Small equipment

Thermometers Laboratory thermometers are routinely checked for accuracy against certified, NIST-traceable thermometers. These calibrations are performed annually for mercury or alcohol in glass thermometers, and quarterly for metal thermometers. Infrared thermometer calibrations are verified daily. Correction factors derived from the annual and quarterly calibrations are applied to temperature readings where applicable. NIST-traceable thermometers are professionally calibrated and re-certified annually.

Balances Calibration checks are performed for each day of use for each balance. The calibration consists of a minimum of two weights which encompass the weight the balance will be used to measure. Calibration weight measurements must meet the acceptance criteria listed in the associated balance calibration log book. Each balance is serviced and calibrated by a certified, professional semiannually. The accuracy of the calibration weights are verified annually.

Volumetric Glassware

All volumetric glassware used at Triangle Laboratories, Inc. must be type "class A". The calibration of each piece of new volumetric glassware is verified gravimetrically prior to the initial production use. Volumetic glassware is never heated or placed in an oven.

Automatic Pipettes

Delivery volumes for the automatic pipettes are checked gravimetrically monthly. Each pipette is checked throughout the volume range of use. Acceptance criteria for continued use is 2% RSD and 97.5 - 102.4% recovery. Pipettes which fail to meet these criteria are tagged and removed from service until repaired such that the criteria is met.

pH Meters

pH meters are calibrated prior to use each day. The meter is calibrated using a single buffer solution at mid-range and the pH of two other solutions (at low and high range) is measured and recorded to verify the accuracy over the range of the meter.

Conductivity Meters

A five point calibration curve using potassium chloride (KCl) solutions is analyzed annually. A single KCl standard solution is used as a check standard each day the meter is used. Acceptance criteria is ±20% of the true value.

Gas Chromatography/Mass Spectrometry (GC/MS) and Liquid Chromatography/Mass Spectrometry (LC/MS/MS)

Tuning and Mass Calibration

For high resolution, selected ion monitoring analyses, the high resolution mass spectrometer is tuned to give the required static resolving power, which is checked by using an oscilloscope. This measurement is confirmed by the use of a data system. The instrument is then mass calibrated using perfluorokerosene (PFK) or perfluorotributlyamine (PFTBA). Mass calibration is adjusted automatically to within ± 5 parts-per-million (ppm) approximately once per second during the course of all quantitative analyses.

The mass calibration of a quadrupole mass spectrometer is checked daily through the use of the perfluorotributylamine reference compound (FC-43/PFTBA). The instrument is adjusted to give specified peak ratios for this compound, consistent with the type of analysis to be performed. The GC/MS is hardware tuned prior to performing the initial and continuing calibrations. Results must meet the peak ratio specifications of the analytical methods. For volatiles analyses, 50 ng of bromofluorobenzene (BFB) is used, and for semivolatiles analyses, 50 ng of decafluorotriphenylphosphine (DFTPP) is used.

Initial Calibration

For environmental samples, the mass spectrometer response is typically calibrated by analyzing a set of five or more initial calibration solutions, as appropriate for each GC/MS method. Typically each solution is analyzed once,

unless the method requires multiple analyses. The relative response factor for each analyte (target compounds, surrogate / internal / alternate standards) is calculated using the expression in Formula 11-1. The mean relative response factor for each analyte is then obtained using the expression in Formula 11-2. Integrated ion currents are utilized for these expressions. An acceptable calibration must meet the method specified criteria for percent relative standard deviations (% RSD) of the mean relative response factors, calculated for each analyte. Failure to meet the criteria will result in corrective action (e.g., locating the source of the problem and adjusting the instrument tuning parameters) before repeating the rejected analysis. Triangle Labs does not analyze any samples unless the performance criteria for calibrations are satisfied.

For pharmaceutical samples, the calibration curve normally consists of a minimum of five standard concentrations analyzed at the beginning and end of the analytical sequence, or are dispersed throughout the analytical run depending on the client's requirements. All standards are used for the regression, with exclusion criteria defined in each method SOP.

Continuing Calibration

For environmental analyses, the initial calibration is verified through the analysis of a continuing calibration standard every 12 hours. The concentration of continuing calibration standard is dependent on the requirements of the specific method. The relative response factors for all analytes of interest are calculated and verified against the initial calibration mean relative response factors. The percent difference (%D) for each analyte is calculated using the expression in Figure 11-3. An acceptable continuing calibration run must have measured percent differences for the analytes within method specified ranges Should any criteria for an acceptable calibration not be met, either instrument maintenance is performed such that a new continuing calibration analysis meets all criteria or a new initial calibration will be established before any samples can be analyzed. No samples may be analyzed unless acceptance criteria have been met.

For pharmaceutical analyses, the calibration is verified through the analysis of quality control samples which are interspersed throughout the analytical sequence. The quality control samples are matrix spikes which contain known levels of analyte and are extracted with the samples.

Formula 11-1

$$RRF = \frac{A_s \times C_s}{A_{is} \times C_{is}}$$

where
RRF = *the relative response factor for the analyte*
A_s = *integrated area or ion current of the internal standard*

A_s = *integrated area or ion current of the analyte*
C_{is} = *amount of the internal standard*
C_s = *amount of the analyte*

Formula 11-2

$$\overline{RRF} = \frac{1}{n}\sum_{i}^{n}\frac{A_s C_{is}}{A_{is} C_s}$$

where: $\overline{RRF}$ = *the mean value of the relative response factors for the analyte*
n = *the total number of data points derived from the initial calibration*
A_{is}, A_s, C_{is} *and* C_s *have the same meaning as in formula 11-1.*

Formula 11-3

$$\%D = \frac{\overline{RRF} - RRF_{cc}}{\overline{RRF}} \times 100$$

where:
$\overline{RRF}$ = *mean relative response factor for the analyte in the initial calibration*
RRF_{cc} = *relative response factor for the analyte from the continuing calibration*

Gas Chromatography/Electron Capture Detector (GC/ECD)

Initial Calibration

Internal standard calibration is utilized for the analysis of pesticides, PCBs and herbicides by GC/ECD. The method-specified number of calibration standards are be used. Each solution is analyzed once and the analyte relative response factors are calculated using the expression in Formula 11-1. The mean relative response factor for each analyte is then obtained by using the expression in formula 11-2. Integrated areas are utilized for these expressions. For multiple response pesticides/PCB's, quantitation consists of an average of the quantitated values for five selected peaks, if possible. The percent relative standard deviation (% RSD) must be less than ±20% in order to use the mean relative response factor for quantitation. If it is greater than ±20%, one more attempt is made to meet criteria. If the second attempt is unsuccessful, the

analyst takes corrective action, such as instrument maintenance, and begins the sequence again.

Atomic Absorption Spectrophotometry (AA)

An initial calibration is performed daily with freshly prepared working standards. A four-point calibration curve is acquired which must have a correlation coefficient of 0.995 or better. The initial calibration is verified every 10 samples or 2 hours, whichever is more frequent. The continuing calibration is required to be within 10% or 20%, depending on the analytical method utilized. Continuing calibration blanks are run at the same frequency. Analysis of samples cannot begin until an initial calibration verification has been performed and is found to be within 10% of the true value.

Inductively Coupled Plasma Emission Spectrophotometry (ICP)

Initial calibration is performed every 8 hours and continuing calibrations are performed every 10 samples or 2 hours, whichever is more frequent. Analysis of samples cannot begin until an initial calibration verification has been performed and is found to be within 10% of the true value. The continuing calibration is required to meet the criteria of the analytical method.

Ion Chromatography (IC)

The ion chromatograph is typically calibrated by analyzing a set of five or more initial calibration solutions, with concentrations of analytes appropriate to the analytical methods. Procedures for verifying the calibration curve are method specific.

AOX/TOX Instrumentation

Instrumentation for the determination of AOX/TOX consists of a column adsorption module, titration cell and combustion/microcoulometric system. Several system performance tests are conducted and must meet acceptance criteria prior to sample analysis. The following performance tests are typically conducted, with slight variations between the different analytical methods. Granular activated carbon utilized in the column adsorption module is tested for purity. The titration cell is tested and adjusted based on the results of an injection of sodium chloride solution. Calibration of the combustion/microcoulometric system is accomplished through the analysis of 2,4,6-trichlorophenol. Verification of system performance and calibration is performed during sample testing according to specifications in the analytical methods.

Sample Analysis Procedures

Techniques for quantitative analysis of samples are specific to the analytical methods and sample matrices. Samples may either be subjected to a series of preparation steps prior to instrumental analysis, or they may be ready for analysis upon arrival at Triangle Labs. Most samples must be analyzed within a defined period of time following their collection, receipt at the lab and/or preparation. These analysis holding times are complied with to the extent possible (samples are

occasionally received near or beyond the expiration date of holding time). Holding times for most methods employed at Triangle Labs may be found in Appendix 4.

After sample analysis is completed and the data is processed, the analyst reviews the resultant data. If established acceptance criteria are not met, corrective action is taken to resolve problems. Once all the samples in a project have been analyzed and the data have met the criteria, the project documentation (instructions, raw data, reports, etc.) is sent to the next stage for preparation of the final report.

Section 12

DATA HANDLING AND SOFTWARE MANAGEMENT

Data Collection and Reduction

Quality assurance principles are applied in the acquisition of raw data related to chemical measurements. Raw data is "primary data" which will be used to generate "secondary" data (the final analytical report). Data can be acquired manually or electronically. Manually acquired data is hand written on data sheets and in logbooks. Electronically acquired data is acquired from an instrument and instrument/computer interface. Specific definitions and data requirements are detailed in the Raw Data SOP.

Manually Acquired Data

Manually acquired data is recorded on data sheets or in notebooks. The data must be recorded immediately by the analyst in permanent ink. Each entry must be signed and dated immediately after entry. Corrections must not obscure any original entries and are made by canceling with one line through the original. Each correction must be dated and initialed by the person who made the correction and a reason for the correction must be stated. Data sheets are standardized, preprinted forms which are subject to document control. Data sheets may be bound into a book or may be used as loose sheets depending on the application. Notebooks are bound, consecutively numbered, and subject to a controlled distribution and archival system.

Electronic Data

Electronically produced data may consist of chromatograms, spectra, data printouts, and raw quantitation reports). The first accepted hard copy report constitutes the raw data for each sample and calibration. Acceptance is signified by the dated signature of the analyst(s),. The accepted hard copy report must contain the full sample ID or calibration name, file name, as well as date and time of acquisition. In the case of inorganic data, all replicate and dilution data is included in the documentation. Any alterations to the raw data hard copies and computer files must be fully documented and clearly attributable to the person making such alterations (e.g., manual integrations are hard-copied for inclusion in the raw data file, with area changes fully documented on the data printouts). No ambiguity in data system printouts as to what peak on a chromatogram corresponds to an analyte of interest is allowed. Computer-collected data is reduced to hard copy as soon as possible. The signed and dated hard-copies of the data files are retained in the project file and are maintained for a minimum of 10 years. The electronic files are safeguarded by a system of disk storage and backup disks to protect loss of data and programs. Software used for data acquisition and quantitation reports is tested according to written procedures to assure that no "bugs" are present.

There are several different means of data collection, review and reduction, which are dependent upon specific methodology and instrumentation. Data review and reduction of pharmaceutical data normally consists of data acquisition via a dedicated computer with further reduction and data reporting utilizing validated spreadsheets. Regression and sample calculations are verified independently for each pharmaceutical data set. Data review and reduction of environmental analyses normally follow the guidelines of relevant EPA reference methods to the extent possible. For HRGC/HRMS analyses, established procedures consist of data acquisition and reduction on a Digital Micro VAX and VAX 3100 and further reduction and data reporting using dBase software on a PC. For HRGC/LRMS analyses, established procedures consist of data acquisition and reduction using PC-based software or a PDP-11/24 system followed by further data reduction and reporting using dBase software. For HRGC analyses, established procedures consist of data acquisition and reduction using PC-based software followed by further data reduction and reporting using dBase software. For AOX/TOX analyses, manual data acquisition from instrument panel readings is followed by data reduction and reporting using spreadsheet software.

All GC, GC/MS, and inorganic data go through several levels of review and inspection, starting with an initial examination in the Instrumentation area, followed by a thorough review in the Report Preparation/Data Review area. After preparation of a report, an independent review is performed by a Chemist other than the one who prepared the report. At each stage of the analytical process, data are reviewed for completeness, adherence to protocol requirements, and credibility. Results are fully validated, possible compromises of data quality are evaluated, and deviations from protocol requirements are documented. To the greatest extent possible, computer programs are utilized for data reduction. Where manual data procedures are required, data review is performed according to standard operating procedures. This ensures that the results are as independent of the chemist performing the duties as possible. Corrective actions are implemented at the earliest possible opportunity.

Data Validation

The tests performed by Triangle Labs typically involve the performance of complex chemical analyses by a number of chemists. For this reason data validation and coordination are very important. At the conclusion of the analyses, data are checked against the original shipping information and analytical request to be sure that the required analyses have been performed on all samples.

The validity of the data are verified through the analysis of blank samples, duplicate samples and matrix spikes. The blank sample results demonstrate the absence of laboratory contamination of the samples. Duplicate analyses give a measure of analytical precision. The analysis of matrix spike samples permits a measure of accuracy. Data for these QC samples are reviewed as soon as possible after analysis. For example, in the inorganic area, a data quality checklist is used by the instrument operator at the time of analysis, to verify that all calibration verifications are within tolerance, and that other QC indicators such as spike recoveries and blanks, are acceptable for a project.

Data Reporting

The data are reported as components identified and the quantities present. The final report includes example calculations and descriptions of the equipment and procedures utilized. Complete data packages of all raw sample and calibration data are be prepared and archived. These are furnished to the client upon request. Sample flagging procedures for HRGC/HRMS analyses are summarized in the final report.. While sample flagging is not done directly on most HRGC/LRMS analytical reports, problematic results are discussed in the case narrative which accompanies each data package. Several standard report formats are used in the inorganic area, tailored to the data structure for the specific project type (e.g., TCLP, Multi-Metals Train or CLP).

Data Package Delivery

Data packages are prepared for delivery by the Shipping and Archive department according to their SOP's. Unless otherwise requested by the client, a copy of the data package is shipped, while the original is retained in a secured archive facility. Reports are fully paginated prior to copying. The data packages are packed to meet the requirements of the commercial carrier chosen for delivery. Packages are delivered by a commercial carrier whose procedures for protecting the data packages are not within the control of Triangle Labs. Should the shipped data package be lost or damaged during delivery, a copy can be quickly prepared as a replacement. Clients are made aware that a commercial carrier will deliver their data packages.

Corrections and Additions to Documentation

The policy for handling additions/corrections of reports already issued is as follows. The Project Scientist requests an addition/correction in writing to the appropriate data review/report preparation personnel, who make the requested change in a timely manner and internally verify the change. An authorized Chemist reviews and approves the addition/correction, and the Data Package Assembly Department mails or faxes the new report, which is then stored with the original data package for a minimum of ten years. In all cases, revised pages are clearly noted as such, as are additional pages added to the report.

Software Management

Triangle Labs has begun a formal validation program of its computer systems. Ultimately, the validation program is intended to be of a level such that all computer systems will meet the scope of any computer system audit. The validation approach is three pronged. First, new software is developed according to appropriate internal validation guidelines. Second, a validation committee has been appointed to oversee specific validation efforts of existing systems. Finally, systems are kept validated through a system of change controls. This includes the *Computer Systems Services Request* (CSSR) forms which employees use to make known to the MIS department, desired changes to software and hardware. CSSR forms include personnel sign-off for each step of the change process; and depending on the nature of the change, specify increasingly stringent required levels of authorization. Change controls also include software version control; changes to existing software are announced, uniquely labeled, documented, and old versions are archived for future reference.

The goals of the software development methodology, existing system validations, and the change control system are to ensure that the software systems perform the required functions accurately, that the users understand how to use the system, and that auditors can assure themselves of the validity of the analytical methods utilized. This in turn insures the ability to deliver accurate analyses in a timely fashion.

Section 13

DOCUMENTATION FOR QUALITY ASSURANCE

Objectives of Documentation

The objectives of documentation for quality assurance are: to provide a standardized, written program of policies, procedures and instructions; to demonstrate that adequate quality assurance and quality control procedures have been implemented; to demonstrate that accountability of the data is maintained; and to ensure traceability of analytical results is facilitated.

Document Control

The laboratory maintains control over the possession and distribution of all documents that directly impact the quality of a product or service. It is the responsibility of area supervisors to ensure that document control files are created and maintained for all applicable documents originating in their areas. This includes, but is not limited to, documents such as the Quality Assurance Manual, Standard Operating Procedures (SOP's), Work Area Guidelines (WAGs), Quality Assurance Project Plans (QAPP's), Analytical Services Guide, client instructions, and product sheets. It also includes standard forms, such as laboratory bench sheets, project communication forms, and corrective action reports.

A written procedure describes document control practices. Full or limited document control is applied, depending upon the purpose of the document. Those publications which document the quality assurance system at Triangle Labs, specifically the QA Manual and Standard Operating Procedures, are subject to full document control practices. Limited document control procedures are employed for other relevant documents, such as forms, flow charts, and price lists. The procedure for limited document control allows for the retention of a previous version for historical information and purposes. Such historical copies are clearly marked as such and can only be used as reference material.

Every document is assigned a unique identification (usually a title, file ID and creation/revision date) which must be present on each page of the document. This unique identification is entered on a master list of documents, along with a distribution list for each document to ensure that pertinent documents are made available wherever they are essential. A master set of current documents is maintained along with the master list.

Full document control, as applied to the QA Manual and Standard Operating Procedures, also includes the following. The status of each document, active/current or inactive/obsolete is indicated on the master list. Each document and any subsequent revisions must be reviewed and approved by authorized personnel prior to issue. Personnel authorized to review and approve a document are to have access to all necessary information on which to base their review and approval. Obsolete documents are to be retrieved from distribution points and replaced with current versions. The nature of changes in documents shall be identified within the document.

Standard Operating Procedures (SOP's)

Standard Operating Procedures (SOP's) are controlled documents in which instructions for every repetitive or standard operations performed by the laboratory are detailed. The author of an SOP should be the person most familiar with the topic being addressed. The standard format for writing SOP's is fully described in the SOP on SOPs. Each SOP is reviewed by senior level staff and authorized by management prior to distribution.

It is important that SOP's receive evaluation and input by laboratory supervisors and key technical personnel. The content of each SOPs must conform to applicable requirements of analytical methods and certification agencies, and be consistent with the Good Laboratory Practice standards. Within these constraints, the content of an SOP may be customized to meet the needs of a particular area of the laboratory. The performance of laboratory operations is subject to audit for compliance with written SOP's. If an SOP is impractical, hard to follow, or no longer meets laboratory needs, it must be modified or replaced.

The need for new or revised SOP's can be determined when a new method is implemented, when the scope of the existing method is extended or when some activities are being performed without adequate SOP's. Such a need can be identified by the analyst involved in the production or by someone from management. Also, the QA Department may identify the need and request new or revised SOP's, usually as a corrective action for deficiencies found during an internal inspection. SOP's are created to provide a clear, concise, description of the procedure with explanatory information to enable a person with the appropriate background to perform the procedure. Revisions are made to SOP's as necessary to reflect changes in procedures.

While area managers are responsible for the operating SOPs, the administrative staff assists with the typing on an as-needed basis. Once technical approval is obtained for a new or revised SOP, the SOP is reviewed by the Quality Assurance Department for compliance with all requirements. The Quality Assurance Department also maintains a database of SOP distribution and version status, as well as maintaining the original copies of each active SOP and the historical files of each out-dated version. The administrative staff distributes copies of the authorized SOPs to area SOP coordinators according to the distribution plan contained in the SOP database. The area SOP coordinator is responsible for discarding copies of obsolete SOPs upon receipt of revisions. Area managers are responsible for training staff in all applicable new or revised SOPs.

Work Area Guidelines

Work Area Guidelines (WAGs) are training documents which entail step-by-step instructions for specific tasks. WAGs are supplements to the SOPs and as such contain additional detail and guidance for handling unusual occurrences. The WAGs are comprised almost entirely of proprietary information and are restricted to use by TLI employees. These documents cannot be distributed to clients or other non-employees.

Quality Records

Quality records must be maintained to prove that the quality assurance system is being effectively applied. At Triangle Labs, specific procedures for the identification, collection, indexing, filing, storage, maintenance, and disposition of various quality records are described in several SOP's.

All quality records must be recorded in permanent (indelible) ink, legible, attributable to those personnel who wrote them, and protected so they may not be adversely affected by an unsuitable environment. They are stored and maintained in a manner that facilitates rapid retrieval for a period of at least ten years after completion. With the exception of internal audit reports, project specific quality records are available for evaluation by the client or his representative during the archive period of ten years. In fact, certain quality records, as specified by SOP or contract, are delivered to the client with the final product.

Project specific quality records are maintained to prove that adequate quality control procedures are being implemented, accountability of the project data is maintained, and traceability of analytical results is facilitated. Accountability means that reported data reflect the sample as it was received, that sample mix-up was avoided, and the sample was properly preserved after receipt. Traceability means that reported data may be reconstructed at a later date. Through proper documentation, a laboratory is able to demonstrate or prove to clients or government agencies that the quality of the data is what the laboratory says it is. Records must contain sufficient information to permit the reconstruction of calibrations, sample preparations and sample analyses.

Quality records that are maintained at Triangle Labs include, but are not limited to, the following.

records for sample receipt, preparation and handling
field sample and quality control sample analysis data
project communication tracking forms
inspection reports for receiving, in-process and final product
subcontractor records
vendor qualification records
logbooks: run logs, maintenance logs, temperature logs, balance logs, etc.
method validation records: MDL studies, initial precision and accuracy demonstrations
recovery data for samples, blanks and spiked samples (maintained in a database)
system and data audit reports
corrective action reports
QA reports to management

Many of these quality records are discussed at length in other sections of this manual. Laboratory notebooks (or "logbooks") are utilized throughout Triangle Labs for many different purposes. All logbooks are maintained according to written procedures. New logbooks are issued by a system of signing them out in a designated logbook. Information that must be documented, both in the new logbook and the sign-out logbook, includes the assigned owner, the date issued, and the name and subject of the logbook. Logbooks must be maintained in accordance with the raw data SOP. Logbooks are kept to document all monitoring, maintenance and calibration of analytical instrumentation, and such laboratory equipment as balances, refrigerators and ovens. Software and hardware records for computers are also kept in logbooks. Logbooks specific to a piece of equipment are kept near that equipment to ensure that the work is recorded concurrently. Logbooks used for personal notes and telephone logs are distributed and tracked in the same manner as laboratory notebooks. Upon completion, all distributed notebooks are stored in the Archive Room for a minimum of ten years.

Archive

The Archive Room is locked at all times and only trained, designated staff have access. All other personnel may enter the room only in the presence of a trained Archivist and must sign and date a logbook in the Archive Room. Any materials removed from the Archive Room must be signed out by the Archivist.

All magnetic and hard copies of data, calibrations, equipment maintenance records, calculations, records of original observations, final test results and any other miscellaneous quality records directly associated with sample analyses are stored in a secured facility for a minimum ten (10) years after completion of a project. They may be stored in the Archive Room or at a secure, off-site storage facility. When completed or no longer in use, logbooks are also archived.

Section 14

QUALITY ASSURANCE

Through a formal quality assurance system, Triangle Laboratories, Inc. is able to prove that products and services meet specific quality standards. These quality standards are defined to meet the needs and requirements of our clients, the analytical methods utilized, government agencies, and senior management of Triangle Labs.

Quality assurance is a very broad and multifaceted concept. It is composed of quality control and quality assessment. Quality control is the most important component of quality assurance. The need for quality assessment would be negligible if the laboratory always achieved perfect quality control.

> *Quality control* is a system of activities applied at each stage of the production process. Its purpose is to assure that products meet defined quality standards. This system includes the following: employee education, training, and experience; documentation (e.g., instructions, document control, records); instrument calibration and maintenance; laboratory accommodations; and inspection.
>
> *Quality assessment* is a system of activities employed to assure that quality control takes place at each stage of the production process. This system includes the following: system, data, and performance audits; reference materials; statistical evaluations; retests; and measurement bias investigation (when measurements may be operator-, instrument-, or methodology-dependent).

The success of a quality assurance system is dependent upon acknowledgment by all personnel of their responsibility for the system. The management of the laboratory is ultimately accountable for product quality, but no one person or group (e.g., the QA Department) is responsible for the greater part of quality assurance program activities. Details of the program may be found throughout this QA manual. The remainder of Section 14 will be limited to a discussion of the Quality Assurance Department, and the major activities performed and/or administered by this group.

The Quality Assurance Department

At Triangle Labs, the QA Department monitors the quality assurance system, as it is implemented throughout the laboratory, and reports the results of its observations to senior management. The Quality Assurance Manager reports directly to the President and the QA Department has no direct responsibility for productivity in the laboratory. The objective of this independence is to eliminate all conflicts of interest in the performance of QA duties. Major activities performed and/or administered by the QA Department are summarized below. Each activity is discussed in greater detail elsewhere in the QA manual, as indicated.

- Performance of internal audits and coordination of external audits (see this section)

- Administration of a system for formal Corrective Action Reports (see this section and Section 15)
- Performance of Quality Assurance Unit (QAU) duties required for GLP-regulated studies (see this section)
- Administration of the system for document control, with emphasis on the maintenance of Standard Operating Procedures (see Section 13)
- Performance of statistical evaluations for selected quality indicators, and maintenance of quality records (e.g., control charts, summary reports) generated to document selected statistical evaluations performed throughout the laboratory (see Section 15)
- Publication of the QA Manual and other documents that describe the quality assurance system at Triangle Labs (see Section 3)

Audits and Inspections

There are several different types of audits. These may be internal, in which the laboratory reviews and examines itself, or external, in which the laboratory is audited by outside organizations, such as accrediting or regulatory agencies and clients.

Internal System Audits

A system audit is an on-site inspection and review of the quality assurance system as it is employed in the laboratory. During an audit, verification may be sought that: adequate written instructions are available for use; that analytical practices performed in the laboratory are consistent with SOP's; that adequate quality control practices are applied during production; that corrective actions are applied as necessary; that deviations from approved protocols are occurring only with proper authorization and documentation; that SOP's, quality records, analytical records, magnetic tape, etc., are properly maintained; and that personnel training records are satisfactory and current.

Internal system audits are implemented by the Quality Assurance Department to assess the functioning of one or more department(s) of the laboratory. These audits consist of real time inspections of the analytical process, comparing the daily operation to the applicable SOPs and policies. Formal inspection reports are issued detailing the extent of the inspection and any non-conformance issues noted. The production staff is required to correct all noted deficiencies and a second acceptable inspection is required for acceptance of the corrections.

Inspection reports may be routed to management at any point in the process depending on the severity of the infraction. Major infractions are reported to management immediately while minor infractions are normally communicated in a summary report dealing with several inspections. The original of each completed inspection report, with management notification dates, is kept on file in the QA files.

External System Audits Representatives of clients, government agencies, and accrediting agencies frequently perform system audits of Triangle Labs. These audits are usually announced inspections, but sometimes are conducted without forewarning. QA Department personnel usually accompany such audit teams through the lab. The auditors receive a brief overview of company objectives, activities, and facilities. Interviews with essential supervisory and technical staff are arranged, along with retrieval of any documentation pertinent to the audit. Auditors typically provide an account of their findings shortly after the audit. This account is evaluated by QA personnel and reported to management, along with recommendations for actions in response to any cited deficiencies.

Data Audits Data audits are performed by technical personnel (in Client Services or the QA Department) on a random sampling of the data reports produced at Triangle Labs. It is a goal to perform a comprehensive evaluation of a representative sampling of data reports. A data report is carefully evaluated for technical, clerical and administrative accuracy. Primary emphasis is placed on the ability of the data report to meet customer requirements. Data audits are utilized for several purposes, including: identification of opportunities for process improvement, evaluation of the efficiency of the system, detection of inadequate execution of quality control procedures, early warning of potential system deficiencies, corrective action recommendations, and reports to upper level management.

Performance Audits A performance audit is the analysis of a fortified blank sample, for the purpose of evaluating laboratory or analyst performance. There are several examples of performance audits, which may be of internal or external origin. Performance Evaluation (PE) samples have analyte concentrations unknown to Triangle Labs, and are submitted by external organizations. PE's may be analyzed as part of multi-laboratory round robin studies, in conjunction with accreditation programs, or as blind check samples submitted by clients. Internal performance audits are fortified blanks with known analyte concentrations, the values of which may or may be known to the analyst. Examples of internal performance audits include initial precision and accuracy studies, QC check samples, laboratory control samples, and blind samples. The results of performance audits are utilized for several purposes other than the evaluation of laboratory performance, including: to fulfill accreditation requirements, to serve as analyst proficiency tests, and to facilitate laboratory improvement efforts.

Non-Conformance Reports

All instances of failure to comply with acceptance criteria are documented in a non-conformance report (NCR). Each report contains a description of the "failure", details of the resulting investigation, and the determined impact on the associated sample(s). Each NCR must be accepted by a member of the quality assurance staff. Original NCRs are maintained as part of the QA records and a copy of the NCR is included in the raw data file of the associated samples. A non-conformance issue may be caused by a particular sample independent of the analytical process or it may have been caused by a faulty analytical process with minimal adverse impact on the particular samples. The staff at Triangle strives to identify both types of situations and deal with them accordingly.

Corrective Action Reports

All major non-routine problems, deficiencies, or irregularities must be reported to management. A formal Corrective Action Report (CAR) system, administered by the QA Department, is in place at Triangle Labs. The QA Department issues CAR forms, monitors the progress of corrective actions, maintains completed documentation, and provides reports to senior management on the status of formal corrective action activities. CAR's may be originated by anyone responsible for the quality of a product. A completed form is sent to an appropriate person or group to whom responsibility for corrective action is assigned. One person is designated the Corrective Action Analyst. This person records the corrective action plans, implementations and follow-up actions completed by the responsible person(s). During the corrective action process, several measures may be taken. These include: determination of the root cause through careful analysis of processes, specifications, quality records, customer complaints, etc., using statistical process control when applicable; implementation of measures that prevent recurrence of the problem; implementation of process controls to ensure that effective corrective action is taken; application of remedial actions to products affected by the identified problem; and revision of documentation for procedures that have undergone change as a result of corrective action.

Certification and Accreditation

Triangle Labs has been granted numerous certifications and accreditations, based upon compliance with standards set forth by the granting agencies. These credentials have enabled Triangle Labs to expand and retain a substantial client base. More information about specific credentials can be found in Section 5, page 3. The nature of the quality assurance program implemented at Triangle Labs is profoundly affected by requirements of certification agencies. The administrative staff is responsible for the administration application and renewal activities associated with the various certification programs, while the QA Department is responsible for the coordination of the technical and quality issues associated with the certification programs. The QA Department is directly responsible for the coordination of:

- On-site audits by outside agencies
- Analysis of blind performance evaluation (PE) samples
- Responses to deficiencies cited in audit reports and performance evaluation results.
- Dissemination of requirements and status of certifications to relevant laboratory personnel.

GLP Regulated Studies

The Good Laboratory Practices (GLP's) are a set of regulations decreed by the United States Environmental Protection Agency (EPA) and the United States Food and Drug Administration (FDA). Compliance with these regulations is required for certain projects ("studies") completed at Triangle Labs. The GLP's define some specific responsibilities for the Quality Assurance Department. Briefly summarized, these QAU duties include the following:

- Maintenance of a copy of the master schedule sheet for all studies

- Maintenance of copies of all protocols pertaining to all studies
- Inspection of each study at adequate intervals
- Preparation of written status reports on each study with reports to management and the study director
- Determination that no deviations from approved protocols or SOP's were made without proper authorization and documentation
- Review of the final study report
- Preparation of a signed statement of the inspections performed and the dates each was reported to management for inclusion in the final study report

Section 15

QUALITY CONTROL

At Triangle Labs, quality control is achieved through the application of a many practices. Quality control activities commence before production is initiated, and are assimilated at each stage of the production process. The purpose of these activities is to assure that all required standards of quality are met. Quality control activities are described in many sections of this manual. The remainder of this section will describe a subset of quality control activities that may be considered a discrete process, summarized as follows:

Prior to the initiation of production activities, required quality standards are defined. These are derived from several sources, including: requirements of the analytical methods, needs stated by the clients, and standards established within Triangle Labs.

During production, verification activities are performed to determine that defined quality standards have been met. Also, preventive measures are applied to avoid the possibility of nonconformity.

When defined quality standards have not been met (nonconformities), corrective actions are applied and verified to determine that the results meet requirements.

Data Quality Objectives

Data are produced for clients at Triangle Labs. Defined quality standards for these data may be expressed as data quality objectives (DQO's). These are established prior to sample preparation and analysis. Quality assurance indicators common to all DQO's include, but are not limited to: accuracy, precision, completeness, representativeness, and comparability. Examination of the QA indicators is performed to demonstrate that the data are scientifically valid, legally defensible and that they adequately meet established DQO's. The QA indicators may be summarized as follows:

Accuracy — A quantitative measure of the relationship of reported data compared to the "true" or expected values. This measurement may be accomplished by evaluation of the recoveries of analytes spiked into samples. Specific accuracy measurement activities include surrogate spikes, matrix spikes and Quality Control Check Samples.

Precision — A quantitative measure of the reproducibility of measurements made under controlled conditions. This measurement may be accomplished by comparison of recoveries of analytes in replicate samples or injections. These analytes may be spiked or native to the duplicate samples. Specific precision measurement activities include blind field replicates, lab replicates, matrix spike replicates and replicate injections

Completeness — A qualitative measure of the amount of valid data obtained from the analytical process compared to the amount that was expected to be obtained. Valid data must meet all data quality objectives for precision and accuracy.

Representativeness — A qualitative measure of the degree to which data represents the characteristics of the population from which samples were collected. This is usually dependent upon sampling techniques not controlled by the analytical laboratory, however, there is representativeness of subsamples prepared within the laboratory from collected samples. Parent samples must be subjected to thorough homogenization prior to subsampling.

Comparability A qualitative measure of the confidence with which one set of data can be compared to another. Characteristics that make comparison possible include standardized report format, consistency of units (e.g., mg/L, ppm), and standardized sample preparation and analysis.

Quality Control Samples and Spikes

Analytical performance is monitored through quality control samples and spikes, such as laboratory method blanks, surrogate spikes, quality control check samples, matrix spikes, matrix spike duplicates, duplicate samples and duplicate injections. Many of these quality control measures, as applied at Triangle Labs, are summarized below.

Laboratory Method Blank A laboratory method blank consists of a sample that is processed in a manner identical to that of a regular sample, except that the matrix is replaced with distilled water for aqueous matrices, sodium sulfate for solid matrices, XAD-2 resin for MM-5 and PUF filter for PUF air sampling cartridges. The laboratory method blank sample is fortified and prepared along with the field samples, at a frequency of one laboratory method blank per batch of 20 (or less) field samples of a given matrix type. The laboratory method blank serves to demonstrate a contamination free environment in the laboratory.

Surrogate Standards For certain methods, all samples, including the laboratory method blank, are spiked with a set of specific surrogate standards to monitor accuracy of the analytical determination for each particular sample. QC criteria for surrogate recoveries are method and matrix specific. Typically, laboratory QC criteria are established upon acquisition of a sufficient number of data points (20 or more) and used for evaluation of sets of data via control charts, while method specified limits are utilized for individual samples.

Quality Control Check Sample A quality control check sample consists of a blank matrix sample which is fortified not only with appropriate internal and/or surrogate standards, but also with target analytes. QC check samples are analyzed at a frequency dependent on the method. They serve as an estimation of system precision and accuracy. Results of QC check samples are monitored on control charts, with QC requirements for recoveries being established as they are for surrogate recoveries.

Matrix Spike Sample A matrix spike (MS) sample consists of a field sample, identified by the client, that is split into two parts and processed in a manner identical to that of the rest of the field samples. However, in addition to the regular fortification with the standards (internal, surrogate and/or alternate), the chemist will add a set of the target analytes to one part of the chosen sample before the preparation. The fortification levels for the target analytes are defined by the analytical method or the client's request. At the request of the client, one such sample will be prepared for every batch of 20 samples (or less) for a given matrix. To be able to run matrix spikes, the client must provide Triangle Labs with extra sample amounts.

The analytical report for the matrix spike will contain a tabulation of the analyte concentrations as expected and as measured, along with the calculated percent recoveries based on the expected concentrations. The percent recoveries actually represent a measurement of the method accuracy for that particular sample and matrix. Accuracy is established and updated for a particular analyte and method. In the absence of observable quantitative interferences, the MS sample showing accuracies falling outside the QC limits must be reanalyzed unless the matrix spike duplicate (MSD), which was processed along with the MS, shows similar deviations as a result of a "matrix effect." This type of corrective action can only be implemented if the sample selected for the MS (and MSD) was proven to be free of the target analytes, or did not contain high concentrations that significantly exceed the MS fortification level of these analytes. "Matrix effect" is further substantiated by acceptable recoveries in a QC check sample processed along with the field samples. Matrix

spike recoveries, and the possible effects on data quality when accuracies fall outside the QC limits, are discussed in the Case Narrative.

Matrix Spike Duplicate Sample

The matrix spike duplicate (MSD) sample is commonly prepared (at the Client's request) in conjunction with the matrix spike (MS) sample. The analytical report will summarize the data from the MS and MSD analyses in a format allowing determination of the precision of the analyses. As for the matrix spike sample, the client must provide Triangle Labs with extra sample amounts.

Duplicate Sample

A duplicate sample (DUP) consists of a set of two identical samples obtained during a single sampling session. At the client's request one such sample per batch of 20 samples (or as specified by the client) per matrix type will be analyzed, provided the client supplies Triangle Labs with the necessary samples.

The analytical report for the duplicate analyses will contain a tabulation of the results showing the precision as relative percent difference (RPD). Precision exceeding any specified target values will necessitate a non-conformance report and an evaluation of the associated data. The influence of the sampling procedure will be included in the data evaluation.

The RPD is calculated as:

$$RPD = \frac{X_1 - X_2}{(X_1 + X_2)/2} \times 100$$

where:

RPD = the relative percent difference

$X_i (i=1,2)$ = the analyte concentration in the original sample (1) and the duplicate sample (2)

Duplicate Injection

Upon client request, a duplicate injection of a single sample extract will be performed. In the absence of observable interferences, the RPD is expected to be within ± 30% or the injections will be repeated after identification of the cause of the poor precision. Field samples analyzed during a suspected out-of-control situation will be reinjected as well.

Statistical Evaluation

Statistical evaluations can be made of selected analytical quality indicators, including spike recoveries, calibration responses, contamination levels, and method detection limits. Production units monitor levels of compliance with many criteria on a "real time" basis. Control charts are used to identify shifts in the analytical process. All identified performance shifts are investigated and causes of adverse shifts are eliminated. Causes of positive shifts are also identified and incorporated in SOPs and staff training as applicable. In-house QC criteria may be determined through historical trend analysis of data collected on QC charts. Statistical evaluations can be performed by both the QA department and production units.

QC Inspection

Quality control inspections are built into the production process. These inspections consist of peer review at each step of the process the ensure compliance with process and product specifications. Acceptance criteria are included in the production SOP's. Written documentation of the analytical process is maintained

beginning with sample receipt and preparation, through instrument calibration, sample analysis, data review and report preparation. This documentation is reviewed for completeness, compliance with written procedures and consistence with client documentation.

Written records of all QC inspections are required indicating the date, inspector and results of the inspection. Detected nonconformances must be recorded during the inspection. Corrective action must be taken and documented whenever nonconformance is detected. The identity of the inspection authority responsible for releasing the product is documented in the inspection records. Until required inspections are performed on the intermediate and final product, it is not permitted to progress further along the production process, except by special, documented, client request.

In-process Inspection and Testing

Each department is responsible for a segment of the production process and for all in-process inspection and testing that takes place within the department. In-process inspection is accomplished through 100% screening for all areas. Each client sample that goes through the analytical process is unique and can be considered a separate lot.

Final Inspection and Testing

The last stage of the production process is the preparation of a final data. This requires a thorough review of all records generated for a client sample set since its receipt, including inspection records and any client documentation that may have originated before sample receipt. A Report Preparation Chemist performs this function during the preparation of the data package. This inspection serves as both an in-process and final inspection of the product. In addition, a second chemist performs another final QC inspection of the data package and quality records. As in any other part of the process, any nonconformances found during these inspections must be documented and corrected before the data package is released. Approval of the data package for release to the client is indicated by the signatures of the Report Preparation and QC Chemists on the case narrative.

Nonconformity

Each field sample that is incorporated into the analytical process is unique. Laboratory procedures are designed to introduce as much standardization as possible. Whenever conformance to standards is uncertain, the product is reviewed to determine the nature and cause of nonconformance. If it is judged to be nonconforming due to the unique nature of a sample, there may be little recourse other than to simply inform the client.

Each case of failure to comply with written acceptance criteria must be recorded in a non-conformance report (NCR). The failure must be recorded by the person who detected or observed it. All investigative efforts are recorded on the NCR with an evaluation of the impact the non-conformance had on the associated samples. Impact on the analytical process is also noted. Recommendations for corrective action are made. A copy of the NCR is kept with the project data. The original NCR is submitted to the QA Department for review and acceptance. Data cannot be reported until all associated NCRs have been accepted by the QA Department

Rework and reanalysis is subject to the same inspection procedures as the initial work. Nonconformity, its review, and its disposition must be documented in the quality records as prescribed by the written procedures.

Corrective and Preventive Action

Appropriate actions must be taken to prevent or correct nonconformities in products and problems in analytical systems. When actions result in permanent procedural changes, pertinent documentation (e.g., SOP's) must also be modified to reflect these changes. Cost-effective preventive measures are applied whenever possible. In specific cases, the cost of applying preventive measures would exceed the cost of

applying routine corrective actions. Because every client sample possesses unique and unknown properties, some predisposition to unpredictable, unpreventable nonconformities exists.

Corrective Action

Specific corrective actions are of two types: routine corrective actions applied to solve minor or commonplace problems, and formal corrective actions taken to eliminate major or non-routine problems.

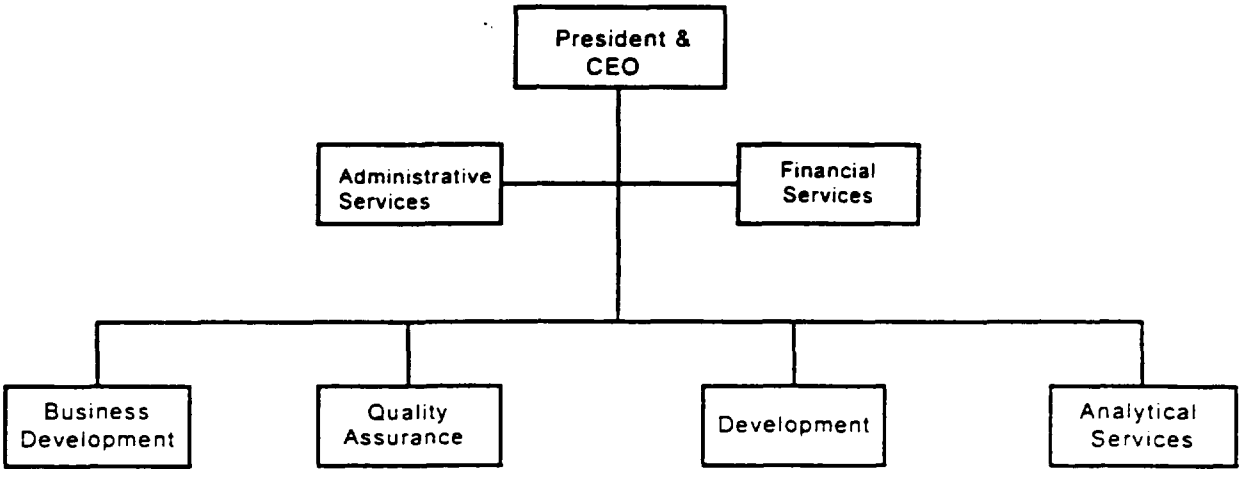
Routine corrective actions are usually made by the chemists, technicians or instrument operators who detect minor problems or product nonconformances. These actions are taken in response to observed non-conformance issues are recorded on the associated NCRs.

There are three procedures for conducting formal corrective actions. The first is corrective action in response to a system audit report from the Quality Assurance Unit. This procedure is more thoroughly described in Section 14, page 2. The second procedure is the formal Corrective Action Report, which may be initiated by anyone who detects a significant quality problem. This procedure is also administered by the Quality Assurance Unit. Further information about it can be found in Section 14, page 3. The third practice is described in a written procedure on "Problem Sample Communication." It is initiated in response to client complaints about specific projects.

Preventive Action

Preventive actions are implemented as part of standard operating procedures, process improvement efforts and corrective actions. When circumstances inherent to a procedure are known to have a high potential for error, the SOP must define measures to prevent the error from occurring. Preventive actions are an integral part of corrective actions, because resultant changes in procedures often prevent recurrence of problems.

Triangle Laboratories, Inc



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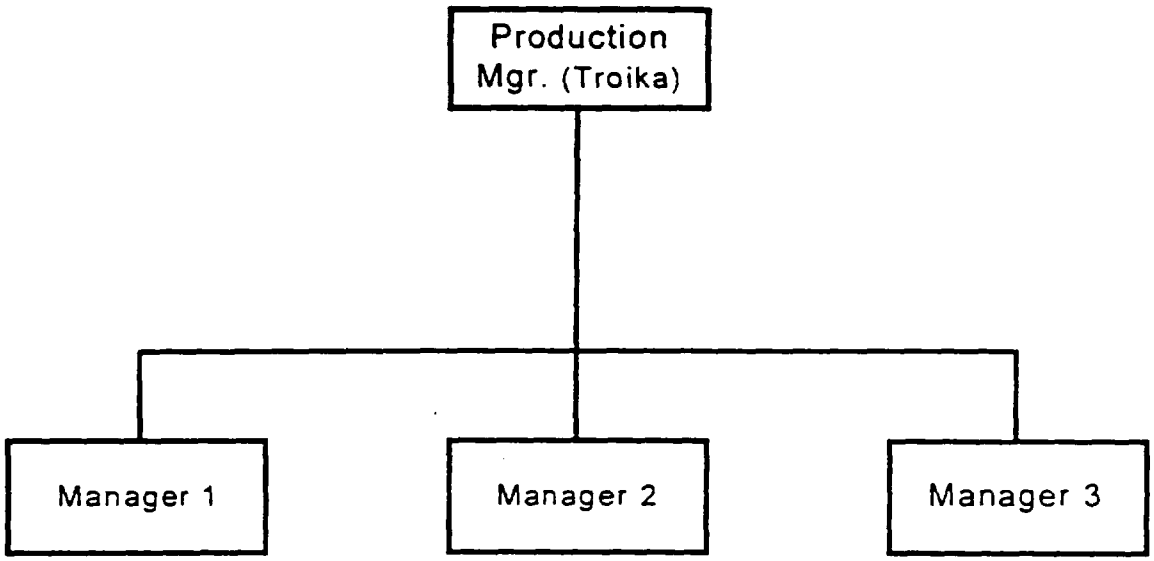
Analytical Services



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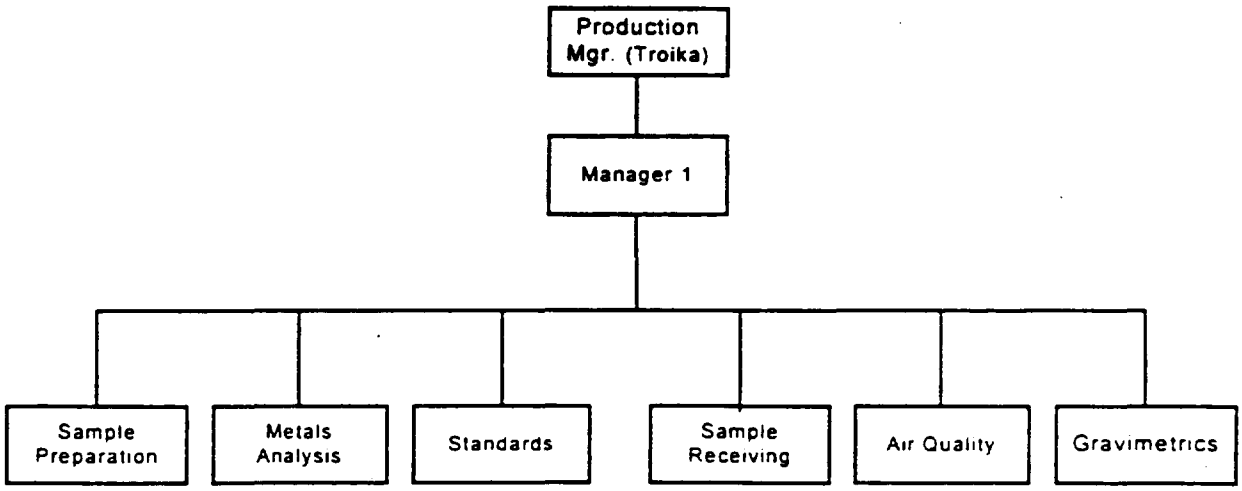

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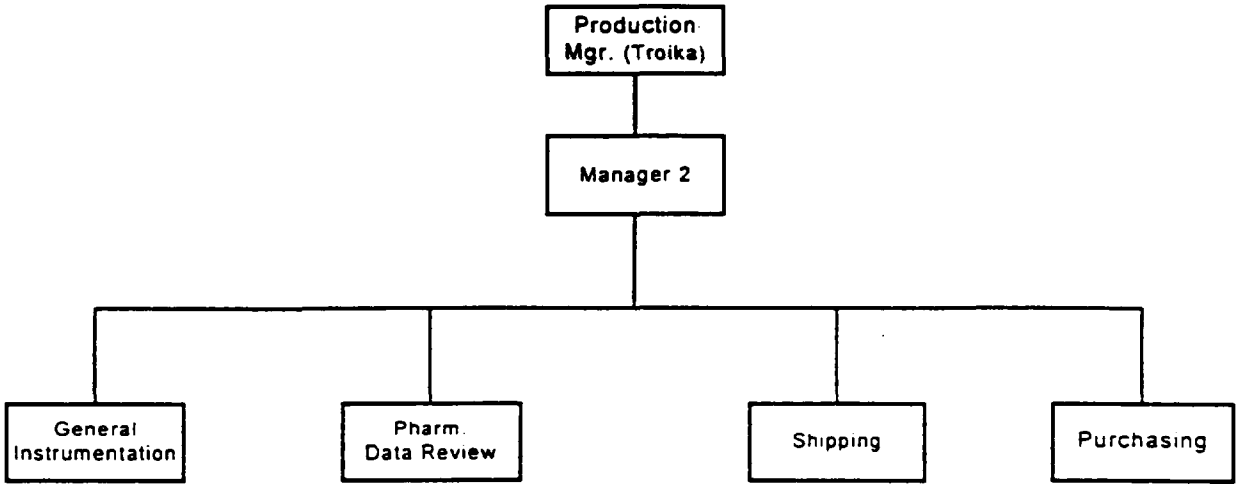

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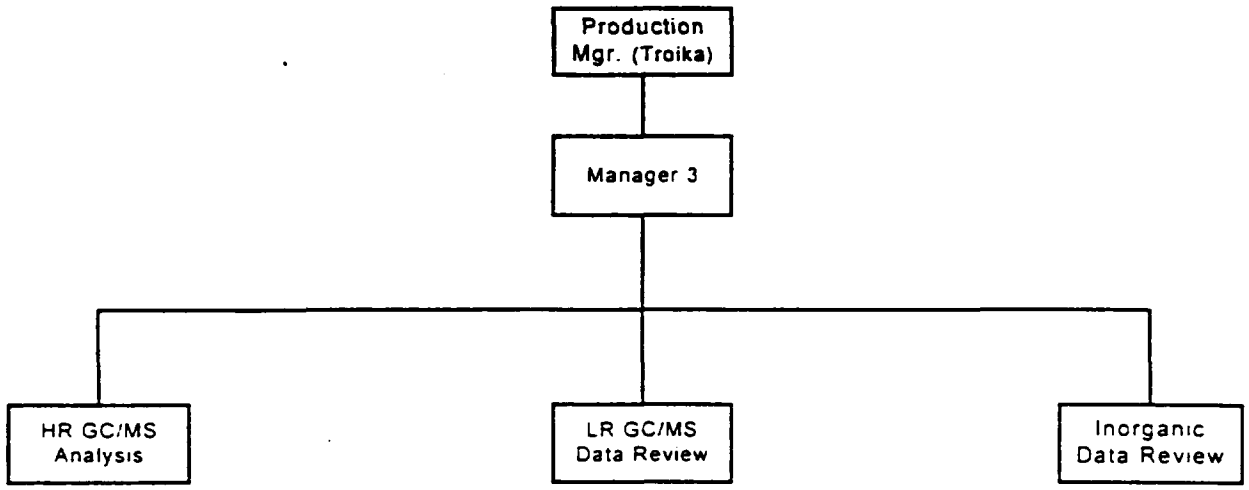

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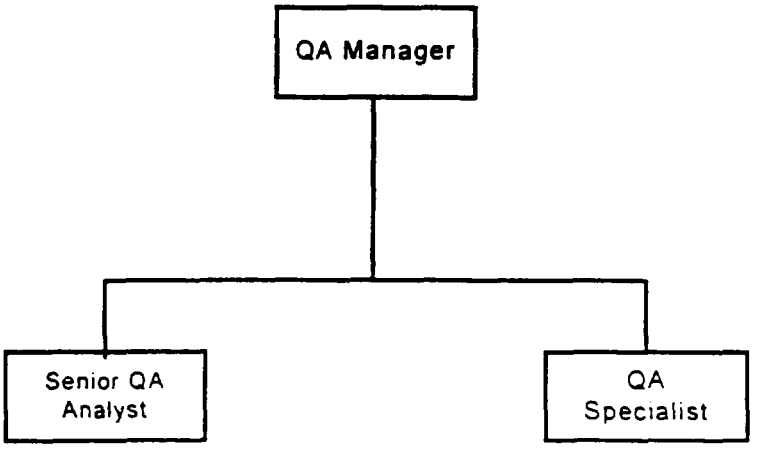

11/11/97 QA

Triangle Laboratories, Inc
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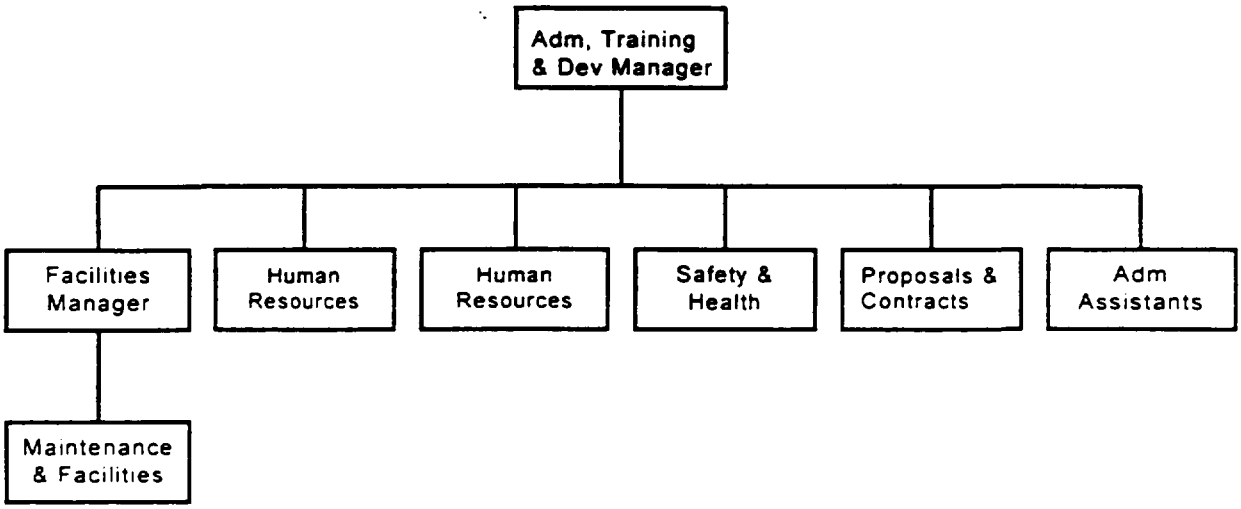

11/11/97 Admin

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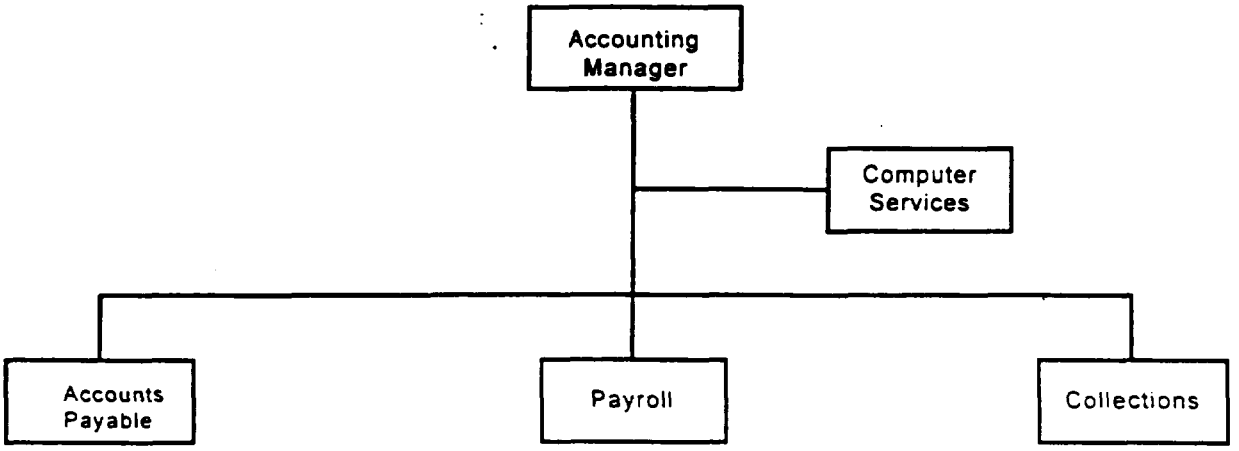

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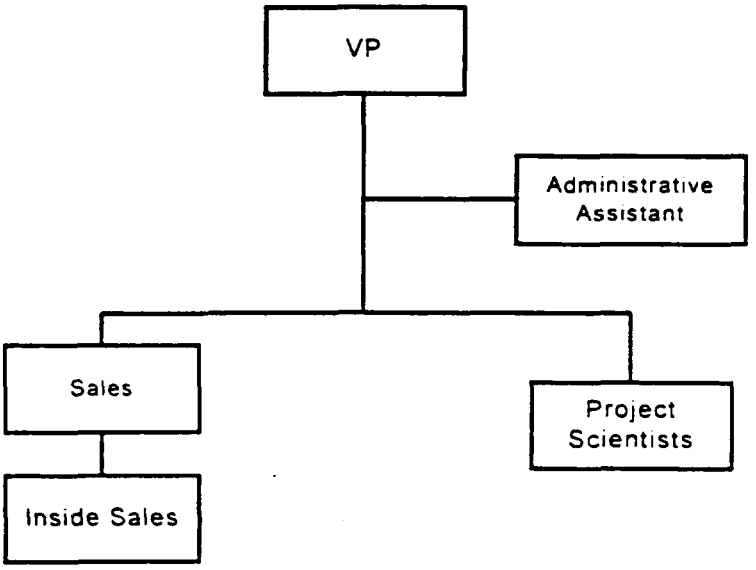
Triangle Laboratories, Inc
New Business Development



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Appendix 2A

VOLATILE COMPOUNDS

Analytes are displayed with the associated internal standard (underlined).

SW-846 Method 8240, Table 2

Bromochloromethane
Acetone
Bromomethane
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
Iodomethane
Methylene chloride
Trichlorofluoromethane
Vinyl chloride
1,2-Dichloroethane-d_4 (surrogate)

1,4-Difluorobenzene
Benzene
Bromodichloromethane
Bromoform
2-Butanone
Carbon Tetrachloride
Chlorodibromomethane
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
4-Methyl-2-pentanone
Styrene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
o-Xylene
m-/p-Xylene

Chlorobenzene-d_5
Chlorobenzene
Ethylbenzene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Bromofluorobenzene (surrogate)
Toluene-d_6 (surrogate)

Non-target compounds known as tentatively identified compounds (TIC's) are identified by a computer generated searcch of the National Institute of Standards and Technology (NIST) Mass Spectral Library.

Appendix 2B

SEMIVOLATILE COMPOUNDS

Analytes are displayed with the associated internal standard (underlined).

SW-846 Method 8270, Table 2

1,4-Dichlorobenzene-d_4
Benzyl alcohol
Bis(2-Chloroethyl)ethene
Bis(2-Chloroisopropyl)ether
2-Chlorophenol
1,4-Dibromobenzene (surr)
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
Hexachlorophenol
2-Methylphenol
4-Methylphenol
N-Nitroso-di-n-propylamine
Phenol
Phenol-d_5 (surr)
2-Fluorophenol (surr)

Naphthalene-d_5
Benzoic acid
4-Chloroaniline
Bis(2-Chloroethoxy)methane
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,4-Dimethylphenol
Hexachlorobutadiene
Isophorone
2-Methylphenol
Naphthalene
Nitrobenzene
2-Nitrophenol
1,2,4-Trichlorobenzene
1,2,5-Trichlorobenzene-d_3 (surrogate)
Nitrobenzene-d_5 (surr)

Acenaphthene-d_{10}
Acenaphthene
Acenaphthylene
2-Chloronaphthalene
4-Chloorophenyl phenyl ether
Dibenzofuran
Diethylphthalate
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluorene
Hezachlorocyclopentadiene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
4-Nitobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2-Fluorobiphenyl (surr)
2,4,6-Tribromophenol (surrogate)

Phenanthrene-d_{10}
Anthracene
Anthracene-d_{10} (surr)
4-Bromophenyl phenyl ether
Di-n-butylphthalate
4,6-Dinitro-2-methylphenol
Fluorene
Hexachlorobenzene
N-Nitrosodiphenylamine
Pentachlorophenol
Phenanthrene

Chrysene-d_{12}
Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate
Butylbenzylphthalate
Chrysene
3,3'-Dichlorobenzidine
Pyrene
Pyrene-d_{10}

Perylene-d_{12}
Terphenyl-d_{14} (surr)
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Di-n-octylphthalate
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene

Non-target compounds known as tentatively identified compounds (TIC's) are identified by a computer generated searcch of the National Institute of Standards and Technology (NIST) Mass Spectral Library

Appendix 2C

DIOXIN/FURAN COMPOUNDS

Table 1- Method 551 Target Analytes

Specific Isomers	Total Isomers
2,3,7,8-TCDD	Total TCDD (22 isomers)
2,3,7,8-TCDF	Total TCDF (38 isomers)

Table 2- Methods 8280, 8290, 23, 1613

Specific Isomers	Total Isomers
2,3,7,8-TCDD	Total TCDD (22 isomers)
1,2,3,7,8-PeCDD	Total PeCDD (14 isomers)
1,2,3,4,7,8-HxCDD	Total HxCDD (10 isomers)
1,2,3,6,7,8-HxCDD	Total HpCDD (2 isomers)
1,2,3,4,6,7,8-HpCDD	
OCDD	Total TCDF (38 isomers)
	Total PeCDF (28 isomers)
2,3,7,8-TCDF	Total HxCDF (16 isomers)
1,2,3,7,8-PeCDF	Total HpCDF (4 isomers)
2,3,4,7,8-PeCDF	
1,2,3,4,7,8-HxCDF	
1,2,3,6,7,8-HxCDF	
2,3,4,6,7,8-HxCDF	
1,2,3,7,8,9-HxCDF	
1,2,3,4,6,7,8-HpCDF	
1,2,3,4,7,8,9-HpCDF	
OCDF	

Appendix 2D

PESTICIDE COMPOUNDS

Method 8081

Aldrin
α-BHC
β-BHC
δ -BHC
γ -BHC (Lindane)
Chlordane (technical)[a]
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide
Methoxychlor
Toxaphene
Aroclor 1016
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
Tetrachloro-meta-xylene (TCMX) - surrogate
Decachlorobiphenyl (DCBP) - surrogate

Appendix 3A

GC/MS ANALYTICAL METHODS: VOLATILES

Matrices	VOST tubes, solids, water
Compounds	See Appendix 2A
Initial Calibration	5 point minimum, SPCC compounds RF > 0.300 (Bromoform RF > 0.250), CCC compounds RSD <30%
Continuing Calibration	mid-level standard analyzed at the beginning of every 12 hours of analysis time, SPCC compounds RF > 0.300 (Bromoform > 0.250), CCC compounds %D < 25% from initial calibration average
Internal Standards	Bromochloromethane 1,4-Dichlorobenzene Chlorobenzene-d_5
Standard Solution Lifetime	Stock Solutions (>1000 ppm): gases in methanol 2 months liquids in methanol 6 months Dilutions (<1000 ppm): in methanol 2 weeks in water 1 week
Holding Time	14 days from sample collection
Validation	Initial performance analysis (water): four (4) 5 mL aliquots composed of reagent water spikes with all analytes at 20 µg/L. Results must meet all method criteria.
QC Check Sample	Blank matrix spiked with equivalent of 20 µg/L all analytes. Must meet all method criteria. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater.

Appendix 3B

GC/MS ANALYTICAL METHODS: SEMIVOLATILES

Matrices	solid waste, soil, water, and air	
Compounds	See Appendix 2B	
Initial Calibration	5 point minimum, SPCC compounds RF > 0.050, CCC compounds RSD <30%	
Continuing Calibration	mid-level standard analyzed at the beginning of every 12 hours of analysis time, SPCC compounds RF > 0.050, CCC compounds %D < 30% from initial calibration average	
Internal Standards	1,4-Dichlorobenzene-d_4 Naphthalene-d_8 Acenaphthalene-d_{10}	Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	Nitrobenzene-d_5 2-Fluorobiphenyl Terphenyl-d_{14} Phenol-d_5 2-Fluorophenol	2,4,6-Tribromophenol pyrene-d_{10} 1,3,5-Trichlrobenzene-d_3 1,4-Dibromobenzene-d_4 Anthracene-d_{10}
Standard Solution Lifetime	Stock Solutions 1 year	
Holding Time	Extraction: water 7 days from sample collection soils 14 days from sample collection Analysis: 40 days from extraction	
Validation	Initial performance analysis (water): four (4) 1 L samples composed of reagent water spikes with all analytes at 100 µg/L, extracted and analyzed. Results must meet all method criteria.	
QC Check Sample	Blank matrix spiked with equivalent of 100 µg/L all analytes. Must meet all method criteria. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater.	

Appendix 3C

GC/MS ANALYTICAL METHODS: DIOXIN/FURAN

	Methods 8290 & 23	**Method 1613**	**Method 551**
Matrices	water, soil, sludge, tissue, pulp, paper, ash, MM5, PUF (Method 23- MM5 only)		
Compounds	See Appendix 2C, Table 2	See Appendix 2C, Table 2	See Appendix 2C, Table 1
Initial Calibration	5 points- 20/25% RSD (Method 23- 25/30% RSD)	5 points- 20/25% RSD	5 points- 20/25% RSD
Continuing Calibration	mid-level standard every 12 hours, 20/25% RPD (Method 23- 25/30% RPD)	Mid-level standard every 12 hours, 20/25% RPD	Mid-level standard at the beginning of every 12 hours and 4th point at the end of injection sequence. 20/25% RPD
Internal Standards	$^{13}C_{12}$-2,3,7,8-TCDD $^{13}C_{12}$-2,3,7,8-TCDF $^{13}C_{12}$-1,2,3,7,8-PeCDD $^{13}C_{12}$-1,2,3,7,8-PeCDF $^{13}C_{12}$-1,2,3,6,7,8-HxCDD $^{13}C_{12}$-1,2,3,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF $^{13}C_{12}$-1,2,3,4,6,7,8-OCDD	same as Method 8290 plus: $^{13}C_{12}$-2,3,4,7,8-PeCDF $^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,7,8,9-HxCDF $^{13}C_{12}$-2,3,4,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	same as Method 8290
Surrogate Standards	$^{13}C_{12}$-2,3,4,7,8-PeCDF $^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF $^{37}Cl_4$-2,3,7,8-TCDD	$^{37}Cl_4$-2,3,7,8-TCDD	same as Method 8290
Standard Solution Lifetime	Based on concentration- ≥10 µg/mL: 15 years, or according to supplier specifications <10 µg/mL: 1 year		
Holding Time	8290 Extract within 30 days of collection; analyze within 45 days of extraction 23 Analyze within 60 days of collection	Water - 1 year at 0-4° C. Solids - 1 year at <-10 ° C.	

Validation	Initial performance analysis (water): four (4) 5 mL aliquots composed of reagent water spikes with all analytes: tetra at 200 pg/L, penta - hepta at 1000 pg/L, and octa at 2000 pg/L.
QC Check Sample	Blank matrix spiked in the same manner as the validation series. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater. (Only 1 per day or once per 20 samples Method 1613)

Appendix 3D

GC/MS ANALYTICAL METHODS: PESTICIDES/PCBs

Matrices	groundwater, soil, non water-miscible waste
Compounds	See Appendix 2D
Initial Calibration	5 point minimum, RSD ≤20%, use average RF
Continuing Calibration	mid-level standard every 10 samples, ≤15% D
Internal Standards	Decafluorobiphenyl 2,4,5,6-Tetrachloro-meta-xylene
Standard Solution Lifetime	Stock Solutions (≥1000 ppm): According to supplier specifications Working Solutions (<100 ppm): 6 months
Holding Time	Extraction: water 7 days from sample collection soils 14 days from sample collection Analysis: 40 days from extraction
Validation	Initial performance analysis (water): four (4) 5 mL aliquots composed of reagent water spikes with all analytes at equivalent of 10 and 2 µg/L. Results must meet all method criteria.
QC Check Sample	Blank matrix spiked with all analytes, equivalent of 10 and 2 µg/L. Must meet all method criteria. Two (2) are analyzed each day of analysis or once per 20 samples whichever is greater.

Appendix 4

CONTAINERS, PRESERVATIVES AND HOLDING TIMES

Parameter	Matrix	Holding time	Recommended Volume	Preservative[d]
Volatile[a] organics	Water	14 days from collection	two 40 mL glass vials with Teflon lined septa, no headspace present	4 drops conc. HCl 4°C
	Soil	14 days from collection	20 g, glass vials with teflon septa, no headspace present	Cool, 4°C
Extractable[b] organics	Water	7 days from collection 40 days from extraction	2.0 L in glass bottles	Cool, 4°C, $Na_2S_2O_3$ if residual chlorine (80 mg/L)
	Soil	14 days from collection 40 days from extraction	100 g in glass jar	Cool, 4°C
AOX/TOX	Water	≥3 days but <6 months after collection	250 mL in glass bottle	HNO3 to pH <2, $Na_2S_2O_3$ if residual chlorine present (20 mg/ 250 mL)
	Soil	≥3 days but <6 months after collection	50 g in glass jar	none
Dioxin	Water	method specific, see Appendix 3C	2.0 L in glass bottles	Cool, 4°C 1613 - $Na_2S_2O_3$ if residual chlorine (80 mg/L)
	Soil	method specific, see Appendix 3C	100 g in glass jar	Cool, 4°C
Metals	Water	28 days Hg 6 months all other metals	0.5 L in glass or plastic	HNO3 to pH <2
	Soil	28 days Hg 6 months all other metals	50 g in glass jar	none

[a]For SW-846: Free chlorine must be removed prior to addition of HCl by exact addition of $Na_2S_2O_3$. Adjust pH <2 for purgeable aromatic hydrocarbons with H_2SO_4, HCl or solid $NaHSO_4$. Adjust pH to 4-5 for acrolein and acrylonitrile.

[b]For SW-846: Preserve phenols, benzidines, nitrosamines, nitroaromatics and cyclic ketones, PAHs, haloethers, chlorinated hydrocarbons and pesticides with 0.008% $Na_2S_2O_3$. Nitrosamines, Nitroaromatics, cyclic ketones and PAHs should be stored in the dark. Pesticides pH=5-9.

[c]For CLP: Dissolved metals require filtration before pH adjustment.

[d]Preservation temperatures are approximate with an acceptable range of ±20C.

TRIANGLE LABORATORIES, INC.
*CONFIDENTIAL and PROPRIETARY INFORMATION

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

TLI SOP No.	DSP105 Version: 15	Effective Date:	July 31, 1998
Author:	Don Harvan	Date Written:	May 4, 1998
Authorization:	Phil Albro (Management)	Date Authorized:	5/27/98

I. **SCOPE AND APPLICATION:** This method provides procedures for the extraction of polychlorinated dibenzo-p-dioxin (tetra- through octachlorinated homologues; PCDDs) and polychlorinated dibenzofuran (tetra- through octachlorinated homologues; PCDFs) from non-tissue solids, including but not limited to soil, sediment, pulp, sludge, paper and/or cardboard, according to SW-846 Method 8290. Only the extraction procedure is contained in this SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear and gloves. Toluene and ethanol are flammable; avoid flames and sparks. The procedure has been validated for either heptane or hexane, since heptane is much less of a health hazard, it should be used instead of hexane whenever possible, but hexane can be used if heptane is unavailable. Do not breathe the vapors, and avoid contact with skin or eyes, as these solvents may cause irritation, nausea, and dizziness. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDS.

NOTES: **Slight procedural differences exist for specified sample types in this SOP. Be careful not to overlook these differences.**

III. **REAGENTS:**

A. Heptane- pesticide grade (< 1 ppm residue)

B. Toluene- pesticide grade (< 1 ppm residue)

C. Ethanol- OmnySolve grade

D. Ethanol/toluene (68/32 v/v) - Take 68 parts (by volume) of Ethanol and mix well with 32 parts (by volume) of Toluene.

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 15	Date Written: May 4, 1998

IV. GLASSWARE PREPARATION

A. All glassware used in this procedure must have been prepared according to glassware washing SOP.

B. The following glassware is needed for each sample:

1. beaker
2. 500 mL or 250 mL flat bottom flask
3. forceps
4. spatula
5. thimble holder - pre-Soxhlet extracted and ready to use
6. Soxhlet extractor - pre-Soxhlet extracted and ready to use

C. If wet sample $\geq$ 15 g, Soxhlet Dean Stark (SDS) extractor must be used in addition to the Soxhlet extractor. Be sure the SDS extractor has been pre-Soxhlet extracted.

D. The flask, thimble holder and Soxhlet or SDS extractor may be 250 or 500 mL, but all pieces must be the same size.

E. If SDS is required, assemble the SDS extractor with stopcock.

F. Rinse all glassware with n-heptane.

G. Label each beaker and flask by placing a color coded sample label on top of a strip of colored lab tape. The colored lab tape is necessary because the adhesive on the color coded labels is difficult to remove from the glass and will cause contamination problems.

H. All flasks require two labels - one on the side of the flask and one on the neck.

V. EXTRACTION PROCEDURE:

A. Plan the extraction batch. An extraction batch can contain up to twenty (20) samples and must include a method blank, a spike pair, and at least one(1) Lab

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
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Control Spike (LCS). Complete the QC batch form, including all samples and QC samples in the extraction batch.

B. Observe and document the physical appearance and consistency of each sample in the wet lab observation log in MILES.

C. Using the percent moisture analysis, determine the amount of sample necessary for a 10 g dry weight sample.

Note: Mix the sample well before taking an aliquot for extraction.

D. For each sample, weigh the amount of sample determined in step VI.C. above. Record the sample weight on the Sample Preparation Management and Tracking Form (SPMFT).

E. Make sure homogeneity is maintained--exclude anything that does not constitute sample's natural matrix.

F. Clean balance by swiping with heptane.

G. Zero balance. Weigh sample and its container.

H. Record the gross weight on the STMF (Sample Tracking and Management Form).

I. Tare beaker in which sample is to be transferred.

J. Record the sample weight on the STMF (Sample Tracking and Management Form). Also indicate with the letter"Y" or "N" if all the sample was used.

(Y)=There is enough sample left to perform re-extraction
(N)=There is NOT enough sample left to perform re-extraction

K. Reweigh sample and its container weight. Record the post-gross weight.

L. Prepare the blank using pre-extracted G-8 filters for pulps and all dried and ground samples. Prepare the blank using pre-extracted sand for all normal ash/sediment/soil/sludge samples. If any laboratory control samples (LCS and/or

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 15	Date Written: May 4, 1998

LCSD) are included in the batch, use the same matrix as Blank. Weigh out 10 grams (± 0.4) for each blank and/or OPR prepared.

M. Check the volume of each standard solution relative to the last volume mark. The bottom of the meniscus must be at the mark.

N. Spike all samples with 20 µL USF-I (0.1µg/mL). Spike any Lab Control Spikes,(LCS/LCSD), Matrix Spikes (MS/MSD) with 40 µL USF-MX (0.01 µg/mL). Record the volume, lot number, concentration and expiration date of each standard on the SPMFT and initial and date the entry. At the end of the spiking process, mark the bottom of the meniscus with a fine point permanent marking pen. Return the standard vials to the storage drawer.

Note: Dioxin standards must be stored at room temperature in amber, glass vials, with Teflon lined septa caps. Spiking instructions can be found in See SOP on Concentration of Extracts Using Rotary Evaporator.

O. After spiking place a glass wool plug on top of the sample in each thimble. Use pre-extracted glasswool.

P. Prepare the Soxhlet apparatus by:

1. Use a 500 mL setup, place 400 mL toluene* in the flatbottom flask. Add 5-6 Teflon boiling chips in each flask.
2. Place the label containing information for the concentration process on the boiling flask on top of the colored lab tape. Write the solvent used on the flask.
3. Place the pre-Soxhleted thimble holder on top of the flask.

Q. ***NOTE:** GP pulp sludge samples require 68:32 ethanol/toluene instead of toluene. GP pulp samples require ethanol instead of toluene. The volume remains 400 mL for 500 mL setup.

R. Place the thimble with the spike sample into the thimble holder. Be sure to seat the thimble at the bottom of the holder.

S. **NOTE:** While the Soxhlet apparatus is sitting on the counter, keep the top capped with aluminum foil to avoid contamination.

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
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T. Place the Soxhlet on top of the thimble holder. If Soxhlet Dean Stark (SDS) is being used, be sure the stopcock is closed.

U. Place the Soxhlet apparatus on the heating mantle and connect the Soxhlet apparatus to the condenser at the ground glass joint. Cap the top of the condenser with aluminum foil.

V. Wrap the thimble holder and Soxhlet extractor with foil. Do not cover the condenser.

W. **NOTE:** If using ethanol as the sole solvent, do not wrap any of the apparatus with aluminum foil.

X. Place a piece of colored tape on the condenser to indicate it is being used for a sample and needs to be pre-Soxhlet extracted after the sample extraction is completed.

Y. If the samples have been designated **high level** write **2X** on the tape. If samples have designated **isolation** write **3X** on the tape.

Z. Turn on the heat. If using a hot plate, use the heat setting #5. If using a six (6) place mantle, use the HIGH setting.

AA. Check the units after one (1) hour. Each unit should be cycling at a rate of five (5) times per hour, have no leaks and have sufficient solvent. Open the aluminum foil on the thimble holder to check the cycling action and close the wrapping. Make adjustments as necessary.

BB. If adjustments were required, check the units again in one (1) hour. Otherwise check again in six (6) hours.

CC. If the weighed sample is >30g, drain the water from the SDS halfway through the extraction (i.e., approximately 8 hours after turning on the heaters).

DD. Extract the sample for 16 hours.

Original stamped in blue: ORIGINAL

TRIANGLE LABORATORIES, INC.
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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

TLI SOP No. DSP105 Version: 15	Date Written: May 4, 1998

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Dioxin Sample Preparation Tracking & Management Form

Project: 91500 Client: Triangle Laboratories, Inc. (TLI01)

Solvent(s)/Acid(s): _____ / _____ / _____ Method: 8290X;Tetra-octa Matrix: _____

Lot Numbers: _____ / _____ / _____ Extraction Date: __/__/__

IS Spike: 20 µl conc: 0.1000 ng/µl
SS Spike: ___ µl conc: _.___ ng/µl
MS Spike: 0 µl conc: 0.0000 ng/µl
LCS Spike: 0 µl conc: 0.0000 ng/µl

								Chemist
								Spike #
								* ID
								* Expir
								* Date
								* Time
								* Conc.
								* Vol.
Sp.Grd	TLI / SAMPLE ID / CLIENT SAMPLE ID	GROSS WEIGHT Before	GROSS WEIGHT After	SAMPLE SIZE g / ml	_____ ng/µl _____ µl	_____ ng/µl _____ µl	_____ ng/µl _____ µl	_____ ng/µl _____ µl
	TLI Blank							Any Left:
000	TLI Matched Blank							yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no
								Any Left
								yes/no

Gross weight of sample container - sample before/after aliquot removal.

Comments: _____

_____

_____

_____ Initials: _____ Date: __/__/__

Initials of both SPIKER AND OBSERVER must be entered. XXXXX = Gross Weight not provided for WATER Samples.

REV 25/27/97 (PSTOP 7)

ATTACHMENT 1

TRIANGLE LABORATORIES, INC.
CONFIDENTIAL and PROPRIETARY INFORMATION

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 15	Date Written: May 4, 1998

Composition of Fortification Standards

USF-I

Analyte	Concentration (µg/mL)
13C, 2,3,7,8-TCDF	0.1
13C, 2,3,7,8-TCDD	0.1
13C, 1,2,3,7,8-PeCDF	0.1
13C, 1,2,3,7,8-PeCDD	0.1
13C, 1,2,3,6,7,8-HxCDF	0.1
13C, 1,2,3,6,7,8-HxCDD	0.1
13C, 1,2,3,4,6,7,8-HpCDF	0.1
13C, 1,2,3,4,6,7,8-HpCDD	0.1
13C-OCDD	0.2

USF-MX

	Concentration (µg/mL)
3-MonoCDF	0.01
3-MonoCDD	0.01
2,3-DiCDF	0.01
2,3-DiCDD	0.01
2,3,8-TriCDF	0.01
1,2,4-TriCDD	0.01
2,3,7,8-TCDF	0.01
2,3,7,8-TCDD	0.01
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.05
1,2,3,7,8-PeCDD	0.05
1,2,3,4,7,8-HxCDF	0.05
1,2,3,6,7,8-HxCDF	0.05
1,2,3,7,8,9-HxCDF	0.05
2,3,4,6,7,8-HxCDF	0.05
1,2,3,4,7,8-HxCDD	0.05
1,2,3,6,7,8-HxCDD	0.05
1,2,3,7,8,9-HxCDD	0.05
1,2,3,4,6,7,8-HpCDF	0.05
1,2,3,4,7,8,9-HpCDF	0.05
1,2,3,4,6,7,8-HpCDD	0.05
OCDF	0.1
OCDD	0.1

USF-C

Analyte	Concentration (µg/mL)
37Cl- 2,3,7,8-TCDD	0.01

ATTACHMENT 2

TRIANGLE LABORATORIES, INC.
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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613, 8290 AND 551

TLI SOP No.	DSP161 Version: 16	Effective Date:	Oct. 23, 1998
Author:	Phil Albro	Date Written:	October 2, 1998
Authorization: Phil Albro (Management)		Date Authorized:	10/18/98

I. **SCOPE AND APPLICATION:** This SOP provides procedures for the extraction of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD and PCDF) from water samples in accordance with methods 1613 or 8290. It may also be applied to the extraction of tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofuran from water in accordance with method 551. See the SOP on Preparation for Extraction of PCDD/PCDF from Water before using the present SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid flames and sparks. Do not breathe the vapors, and avoid contact with skin and eyes. They may cause irritation, nausea, dizziness, and, in extreme cases, death. For additional safety and health information, see the TLI Safety and Health Manual and the appropriate MSDS.

III. **REAGENTS:**

A. Organic-free reagent water- Either Dracor or Fisher HPLC Grade

B. Heptane-pesticide grade or better quality, less than 1 ppm residue on evaporation.

C. Sodium sulfate-anhydrous, pesticide grade.

D. Methylene Chloride-pesticide grade or better quality.

E. Toluene-pesticide grade or better quality.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

IV. GLASSWARE PREPARATION:

A. All glassware used in this procedure must have been prepared according to the SOP entitled "Glassware Cleaning".

B. The following glassware is needed for each sample:

2 L separatory funnel with stopper and Teflon© stopcock

A. 1000 mL graduated cylinder

medium glass powder funnel

250 mL round bottom flask

500 mL extraction flask and regular thimble holder (pre-Soxlet extracted).

Soxlet extractor (pre-Soxlet extracted).

Soxhlet Dean-Stark (SDS) extractor - pre-soxhlet extracted and ready for use

A. Assemble the separatory funnel(s) with stopcock and stopper.

B. Rinse the following with heptane:

separatory funnel(s)

graduated cylinder(s)

all flasks

glass powder funnel(s)

A. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a waste container.

B. After rinsing, invert all flasks and allow to fully drain.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

C. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

I. **SEPARATORY FUNNEL EXTRACTION PROCEDURE:**

A. If has not already been done in the preparation of the sample for extraction, pour the sample volume into a 2 L separatory funnel. Rinse the sample bottle with 60 mL of methylene chloride and transfer to the separatory funnel.

B. Extract the aqueous phase with methylene chloride as follows:

1. Shake the separatory funnel with water sample and methylene chloride for 5 minutes using Glas-Col Automatic Shaker (or 2 minutes by hand). Be sure to vent the funnel periodically to avoid pressure buildup.

Note: If using the Gas-Col shaker, set the timer for 5 minutes and turn the power on. Slowly increase the speed to 40 or the maximum speed possible without displacing any sample through the vent.

Allow the solvent layers to settle for 10 minutes. If emulsions occur, filter the water + emulsion through a G8 filter or glass wool with a methylene chloride rinse. Add the methylene chloride rinses to the methylene chloride extract.

2. Drain the methylene chloride layer through anhydrous sodium sulfate into a 250 mL flask.

3. Repeat steps 1-3 two more times using 60 mL methylene chloride for each extraction. A total of three extractions are required for each sample.

1. Rinse the sodium sulfate twice with 10 mL methylene chloride. Collect the methylene chloride rinses in the 250 mL flask containing the sample extract.

I. **EXTRACTING THE FILTER:**

A. Soxhlet extract the filters, glasswool used to break emulsions, and all filtered solids as follows:

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

1. Place filters in a toluene pre-Soxhlet extracted thimble (500 mL size).

2. For methods 1613 and 8290, add 375-400 mL of toluene to the 500 mL boiling flask; For method 551, use 400 mL of ethanol: toluene 68:32 (v/v) to the 500 mL flask.

3. Add 5-6 Teflon boiling chips to the boiling flask.

4. Place the label containing information for the concentration process on the boiling flask on top of colored lab tape. Write solvent used on flask with marker.

a) Do not place set up on hotplates until extraction of the water phase is completed to insure no additional emulsions need to be filtered and the filter or glasswool placed into the thimble with the first filter.

2. Extract using pre-Soxhlet extracted Soxhlet apparatus for 16 hours.

3. After extraction, let cool and ensure the label indicating that this extract is to be combined with the methylene chloride extract from the water phase is still intact.

II. CONTINUOUS LIQUID-LIQUID EXTRACTION PROCEDURE:

Note: The use of the continuous liquid-liquid extractor is always allowed as an alternative to separatory funnel extraction in method 8290. It is the technique of choice when a given sample type is known to produce difficult emulsions. Use this technique with methods 1613 (A or B) and 551 whenever a re-extraction is needed because of low recoveries during the separatory funnel extraction step. Be sure to indicate on the extraction form whenever L-L extraction was used.

Note 2: The L-L extractor simply substitutes for a separatory funnel; therefore all considerations of filtering, determination of solids or particulate solids, or water vs. sludge described in the SOP on Preparation for Extraction of PCDD/PCDF from Water for Methods 1613, 8290 and 551 still apply.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

A. Assemble Glassware

1. Using pre-extracted glassware, rinse the extractor body and 500 mL flat bottom flask with methylene chloride. Discard rinse as waste.

2. Place 5-6 methylene chloride pre-extracted boiling chips in the flat bottom flask. Add approximately 250 mL of clean methylene chloride to the flask.

3. Add approximately 150 mL of methylene chloride to the extractor body.

4. Attach extractor body to the flask with green plastic clamp.

5. Label flat bottom with solvent, project number and sample number using color labels.

B. Preparation of Water Sample

1. Measure and record 1 liter of Reagent water each for blank and either OPR (1613), or LCS/LCSD (8290) utilizing a 1000 mL graduated cylinder.

2. Measure 1000 mL of well mixed sample and transfer to the extractor body. Record this volume on the sample preparation and tracking form. Note: If the sample does not contain 1000 mL, record the volume it does contain, but make up the difference with Reagent water. The L-L apparatus needs 1000 mL of water to operate correctly. The sample size to use in calculations, however, is the actual sample size not including make-up water.

3. Rinse the 1000 mL graduated cylinder three times with 20 mL methylene chloride and transfer rinses to the extractor body.

C. Extraction

1. Place Continuous Liquid-Liquid setup on condenser/hot plate and seat securely in place. Use aluminum foil shimmies to align body vertically and to fill any space between hotplate and bottom of the flask.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

2. Turn hotplate on to 400 degrees.

3. Extract for 18 hours.

4. Dismantle setup after they have cooled. Keep only the methylene chloride in the flat bottom flask.

5. Discard water and methylene chloride in extractor body as waste.

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EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280, DFLMO1.1 AND 613

TLI SOP No. DSP224	Version: 10	Effective Date:	November 10, 1998
Author:	Sylvie Kiaku	Date Written:	March 13, 1998
Authorization: Phil Albro (Management)		Date Authorized:	11/9/98

I. **SCOPE AND APPLICATION:** The purpose of the SOP is to describe soxhlet extraction of PCDD/PCDF from solid samples using methods 8280 and DFLMO1.1.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid sparks and flames. Avoid contact with skin and eyes. Avoid breathing vapors. They may cause irritation, nausea, dizziness, and in extreme cases, death. For additional safety information, see TLI Safety and Health Manual and appropriate MSDS.

III. **REAGENTS:**

- Toluene- Pesticide grade or better quality.
- Sodium sulfate- powder, anhydrous, pre-extracted with methylene chloride
- Tridecane- Sigma, carbon filtered.
- Filtered n-heptane

IV. **GLASSWARE PREPARATION:**

Each extraction setup requires:

A. 150 mL or 250 mL beaker

B. 500 mL flat bottom flask, pre-extracted

C. small or large (depending on availability) thimble holder, pre-extracted

D. scintillation vial

EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280, DFLMO1.1 AND 613	
TLI SOP No. DSP224 Version: 10	Date Written: March 13, 1998

E. spatula

V. For method **DFLMO1.1** samples, also:

A. Dean-Stark apparatus, pre-extracted

B. Rinse every item from the above list with hexane or heptane.

C. After rinsing invert all flasks, thimble holders, etc. and allow to fully drain.

D. Label each container by placing a color coded sample label on top of a strip of colored tape.

NOTE: All flat bottom flasks require two labels with sample ID - one on the side of the flask and one on the neck. Also, place on the flask a label, or write with a marker, name of the solvent inside and the next step.

1. Add 400 mL of toluene and 5-6 boiling chips to the boiling flask. Place thimbleholder in the mouth of the flask.

2. Place small or large (depending on availability) pre-extracted thimble in the beaker.

VI. **EXTRACTION PROCEDURE:**

A. **NOTE:** Percent moisture should be determined for each sample before the extraction step.

1. Remove the samples from storage (cooler) and place them on clean aluminum foil laid out on a lab bench. Allow sufficient time for samples to reach ambient temperature.

2. Check sample IDs on sample containers against sample IDs on the Sample Preparation Tracking and Management Form. If there are any discrepancies contact the Project Manager for further instructions.

3. Take gross weight of sample container and record on Sample Preparation Tracking and Management Form (SPTMF) in folder.

EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280, DFLMO1.1 AND 613	
TLI SOP No. DSP224 Version: 10	Date Written: March 13, 1998

4. Open sample jar and mix sample thoroughly with a solvent rinsed spatula. Place beaker with pre-extracted thimble on the calibrated scale, and tare the scale.

5. Using spatula, transfer scoops of sample to the thimble, until about 10 g (wet weight) has been delivered for extraction. Do not transfer rocks, glass, organic matter or any other debris unless the entire sample is debris.

   NOTE: Use 10g of sodium sulfate for blank and any LCS/LCSD samples.

6. Record the weight of extraction sample in the MILES and on the SPTMF.

7. Record observations of the physical appearance of samples in MILES (Wet Lab Observation menu).

8. Weigh sample container and record the weight on SPTMF.

9. Add ~30 g or more of anhydrous sodium sulfate to the thimble. The amount depends on the moistness of the sample. The wetter the sample, the more sodium sulfate that must be added.

10. Mix the sample and the sodium sulfate thoroughly inside the thimble.

11. Spike all samples in the extraction batch with 100 µL of 8280 Internal Standard at 0.5 µg/mL. Spike any LCS/LCSD and/or MS/MSD samples with 250 µL of 8280 Matrix Spike at 0.1µg/mL - for **Method 8280** samples, and for **Method DFLMO1.1** samples (see attachment for spiking table). For method 613 spike all samples with 100 µL of 613 internal standard at 0.5 µg/mL. Spike any LCS/LSCD and /or MS/MSD with 250 µL of 613 matrix spikeat 0.1 µg/mL Spike directly into the sample. Record the volume, lot number, concentration and expiration date of each standard added to the samples.

12. Place the thimble in the Soxhlet extractor, place the Soxhlet extractor on the heating mantle, connect with the condenser.

    NOTE: Dean-Stark apparatus must be added to Soxhlet extractor for all method **DFML01.1** samples.

EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280, DFLMO1.1 AND 613	
TLI SOP No. DSP224 Version: 10	Date Written: March 13, 1998

13. Cap the top of the condenser with aluminum foil. Wrap the thimble holder and Dean-Stark extractor with foil. Place a piece of colored tape on the condenser to indicate it is being used for a sample and needs to be pre-extracted after the sample extraction is completed. Write **3X** on the tape.

14. Adjust the heat so the solvent cycles completely through the system at least 5 times per hour.

15. Check units after one hour. Each unit should be refluxing, have no leaks and have sufficient solvent. Make adjustment as needed. If adjustments were required, check the units again in one hour. Otherwise, check again in six hours.

16. Extract sample for 16 hours.

17. After 16 hours turn off the heater. Allow the sample to cool off for 20-30 minutes. Drain and discard water from SDS trap.

18. Remove flat bottom flask. Discard toluene from thimble holder and SDS into the appropriate waste container. The extract is ready for concentration.

VII. CONCENTRATION AND DIVIDING PROCEDURES:

A. Add 500 µL of carbon filtered Tridecane to the flask with the extract.

B. Concentrate the sample to 0.5 mL in the rotary evaporator at a temperature of 42-45°C.

C. Solvent exchange the sample twice with 20 mL of heptane or iso-octane if heptane is unavailable.

D. Add 10 mL of hexane to the sample flask, sonicate well.

E. Transfer the extract to a scintillation vial calibrated to 20 mL. Rinse the sample flask twice with 5 mL of heptane, add rinses to the vial.

F. Adjust volume in the vial to exactly 20 mL, mix well then immediately transfer required portion (usually 20% - 4 mL) back to the original flask.

EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280, DFLMO1.1 AND 613	
TLI SOP No. DSP224 Version: 10	Date Written: March 13, 1998

G. Spike the sample portion in the flask with 100 µL of 8280 Surrogate Standards at 0.05µg/mL, and relinquish to cleanup room. For method 613, spike the sample with 20µL of 613 surrogate standard at 0.014 µg/mL.

H. Mark the level of the sample extract remaining in the scintillation vial. Archive the sample extract in the cooler #2.

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EXTRACTION OF PCDD/PCDF FROM SOLID SAMPLES - 8280, DFLMO1.1 AND 613	
TLI SOP No. DSP224 Version: 10	Date Written: March 13, 1998

SAMPLE FORTIFICATION FOR METHODS 8280, DFLMO1.1 AND 613

METHOD 8280

Internal Standard (8280-I)	100 µL	0.5 µg/mL
Surrogate Standard (8280-C)	100 µL	0.05 µg/mL
Matrix Spike (8280-MX)	250 µL	0.1 µg/mL

DFLM01.1

Internal Standard	100 µL	0.5 µg/mL
Surrogate Standard	100 µL	0.5 µg/mL
Matrix Spike	250 µL	0.1 µg/mL

METHOD 613

Internal Standard	100 µL	0.5 µg/mL
Surrogate Standard	20 µL	0.014 µg/mL
Matrix Spike	100 µL	0.1 µg/mL

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PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A			
TLI SOP No. DSP289	Version: 1	Effective Date:	2/12/99
Author:	Sylvie Kiaku	Date Written:	December 7, 1998
Authorization: Phil Albro (Management)		Date Authorized:	2/5/99

I. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the procedure for extracting PCDD and PCDF from water samples using Methods 8280A.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid flames and sparks. Do not breathe the vapors, and avoid contact with skin and eyes. They may cause irritation nausea, dizziness, and, in extreme cases, death. For additional safety and health information, see the TLI Safety and Health Manual and the appropriate MSDS.

III. **REAGENTS:**

A. Acetone, Optima Grade

B. Methylene Chloride, Optima Grade

C. n-Heptane, Low Residue Grade

D. Anhydrous Sodium Sulfate, Pesticide Grade

E. Organic Free Reagent water (HPLC water)

F. Carbon-filtered Tridecane

G. Toluene, Optima Grade

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
TLI SOP No. DSP289 Version: 1	Date Written: December 7, 1998

IV. GLASSWARE PREPARATION:

The following glassware is needed for each sample:

- 1 2 L separatory funnel with stopper and stopcock
- 1 1000 mL graduated cylinder
- 1 glass powder funnel
- 1 250 mL Erlenmeyer flask or 250 mL round bottom flask
- 1 1000 mL side arm suction flask
- 1 Buchner funnel
- 1 500 mL extraction flask
- 1 Soxhlet extractor (pre- extracted)
- 1 Soxhlet Dean-Stark (SDS) extractor (pre- extracted)

* if large amount of solids present in sample, proceed with continuous liquid-liquid procedure. (See SOP #DSP278)

A. Assemble the separatory funnel(s) with stopcock and stopper.

B. Rinse the following with n-heptane:

- separatory funnel(s)
- graduated cylinder(s)
- scintillation vial
- all flasks
- Buchner funnel(s)

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
TLI SOP No. DSP289 Version: 1	Date Written: December 7, 1998

- glass powder funnel

C. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a waste container.

D. After rinsing, invert all flasks and allow to fully drain.

E. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

F. For sample filtration, place a Gelman Type A filter in each Buchner funnel with a G8 glass filter on top. Place the Buchner funnel in the mouth of the suction flask.

G. Label each flask, separatory funnel, and scintillation vial by placing a color coded sample label on top of a strip of colored lab tape. Also, write on the flask with a marker, the name of the solvent used and next step(s) (see ATTACHMENT 1).

NOTE: All extraction flasks require two labels with the sample ID - one on the side of the flask and one on the neck.

V. EXTRACTION PROCEDURE:

A. Plan the extraction batch according to the SOP on batching projects. An extraction batch can contain up to twenty (20) samples and must include a method blank, a spike pair, and at least one (1) Lab Control Spike (LCS) and one Lab Control Spike Duplicate (LCDS). Complete the QC batch form, including all samples and QC samples in the extraction batch.

B. Remove the samples from storage (cooler) and place them on clean lab bench. Allow sufficient time for samples to reach ambient temperature.

C. Check sample IDs on sample containers against IDs on Sample Preparation Tracking and Management Form. If there are any discrepancies contact the Sample Custodian and/or the Project Initiator for further instructions.

D. Shake each sample bottle for one minute. Mark the volume of the sample on the original container using a marker.

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
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Note: An aliquot cannot be taken of an aqueous sample. The entire contents of the bottle must be used.

E. Use 1000 mL of HPLC water for the blank, LCS and LCSD, and transfer each of them into a clean one liter amber bottle.

F. Save all original sample containers in order to measure the sample volume at the end of the extraction.

G. Once the extraction is complete, fill up all the original sample containers with water up to the mark.

H. Measure and record sample volume in the folder and in the Wet Lab Oservation menu in MILES. Discard the water, then discard the bottles.

I. Record pH and observations of physical appearance of samples (i.e. color, viscosity) in the Wet Lab Observation menu in the Miles. If pH is greater than 9, adjust pH to 7-9 with sulfuric acid.

J. Add approximately 1 mL of acetone to each scintillation vial. Check the volume of each standard solution relative to the last volume mark. The bottom of the meniscus must be at the mark. Add appropriate standards to each vial (see Sample Preparation Tracking Form and ATTACHMENT 2). Record the volume, lot number, concentration and expiration date of each standard added to the vials.

K. At the end of the spiking process, mark the bottom of the meniscus with a fine point permanent marking pen. Return the standard vials to the storage drawer.

Note: Dioxin standards must be stored at room temperature in amber, glass vials, with teflon lines septa caps.

L. Ensure the spike has been well mixed into the acetone, then transfer, using Pasteur pipettes with yellow bulbs, as close to 100% as possible of the acetone solutions to their respective samples. Cap the sample bottles and shake vigorously for one (1) minute to mix, then let stand for approximately 30 minutes.

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
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M. If the bottle is so full you can not add the spike, transfer 5 mL of water from the top of the bottle into the separatory funnel assigned to that sample, then spike the remainder.

N. Filter each sample using the suction filtering system. If residues remain in the sample bottle, rinse the sample bottle and separatory funnel with 50 mL HPLC water and also filter. Transfer the filtered sample back into the 2 L separatory funnel.

O. Soxhlet extract the filters and all filtered solids from step V.L as follows:

1. Place filters in a toluene pre-Soxhlet extracted thimble.

2. Add toluene and 5-6 Teflon boiling chips to the boiling flask (375 mL of solvent for a 500 mL flask).

3. Place the thimble in Soxhlet extractor and reflux for 16 hours. The solvent must cycle completely through the system at least 5 times per hour. Use SDS extractors for all samples.

4. After 16 hours turn off the heater. Allow sample in toluene to cool off for 20-30 minutes.

5. Remove flat bottom flask. Discard the toluene from SDS side arm and from thimble holder into the appropriate waste container. The extract is ready for concentration.

P. Extract the aqueous phase of the sample with methylene chloride as follows:

1. Add 60 mL methylene chloride to the empty sample bottle. Cap the bottle and shake for 30 seconds to rinse the inner surface. Transfer the methylene chloride to the filtration flask and finally to the separatory funnel.

2. Shake the separatory funnel containing the water sample and methylene chloride for 2 minutes by hand. Make sure to properly vent the separatory funnel for excess gas pressure.

3. Allow the organic layers to settle for 10 minutes.

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
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NOTE: If emulsions occur, filter through glasswool and collect the filtrate to be added back to the separatory funnel. Always treat the blank in the same manner as the sample(s). If a sample requires treatment for emulsion, the associated blank must receive the same treatment.

4. Drain the methylene chloride layer through anhydrous sodium sulfate into a 250 mL flask.

5. Repeat steps 1-4 above two more times using 60 mL methylene chloride for each extraction. A total of three extractions are required for each sample.

6. Rinse the sodium sulfate three times with 10 mL methylene chloride. Collect the methylene chloride rinses in the 250 mL flask containing the sample extract. The extract is ready for concentration.

VI. CONCENTRATION AND DIVIDING PROCEDURES:

A. Concentrate the extracts using a rotary evaporator as follows:

1. Add 500 µL of carbon filtered tridecane to the flask containing the toluene extract and rotary evaporate to 0.5 mL combining with the methylene chloride portion of the sample.

B. Solvent exchange each sample twice with 20 mL of heptane or with Iso-octane. Concentrating the extract to approximately 0.5 mL each time.

NOTE: Iso-octane may be substituted for n-heptane.

C. Add 10 mL of n-heptane to the sample flask, sonicate well for about one minute.

D. Transfer the extract to a scintillation vial calibrated to 20 mL. Rinse the sample container two times with 5 mL of n-heptane, add rinses to the vial.

E. Adjust volume in the vial with heptane to exactly 20 mL, mix well then immediately transfer required portion (usually 20% - 4 mL) back to the original flask.

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
TLI SOP No. DSP289 Version: 1	Date Written: December 7, 1998

F. Spike the sample portion in the flask with appropriate surrogate standards (see Sample Preparation Tracking Form and ATTACHMENT 2), and relinquish to cleanup room.

G. Mark the level of the sample extract remaining in the scintillation vial. Archive the sample extract in cooler #2.

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PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
TLI SOP No. DSP289 Version: 1	Date Written: December 7, 1998

EXTRACTION FLASK LABELING:

a.	boiling flask	Toluene Add Tridecane Combine
b.	flask with Methylene Chloride extract	Methylene Chloride Combine

ATTACHMENT 1

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
TLI SOP No. DSP289 Version: 1	Date Written: December 7, 1998

SAMPLE FORTIFICATION FOR METHOD 8280A

METHOD 8280A	Amount	Concentration
Internal Standard (8280-I)	100 µL	0.5 µg/mL
Surrogate Standard (8280-S)	100 µL	0.05 µg/mL
Matrix Spike (8280-MX)	250 µL	0.1 µg/mL

ATTACHMENT 2

PCDD/PCDF EXTRACTION IN WATER - METHOD 8280A	
TLI SOP No. DSP289 Version: 1	Date Written: December 7, 1998

Composition of Fortification Standards

8280-I

Analyte	Concentration (µg/mL)
13C, 2,3,7,8-TCDF	0.5
13C, 2,3,7,8-TCDF	0.5
13C, 1,2,3,6,7,8-HxCDD	0.5
13C, 1,2,3,4,6,7,8-HpCDF	1.0
13C-OCDD	5.0

8280-C

Analyte	Concentration (µg/mL)
37Cl- 2,3,7,8-TCDD	0.1

8280-MX

	Concentration (µg/mL)
2,3,7,8-TCDF	0.1
2,3,7,8-TCDD	0.1
1,2,3,7,8-PeCDF	0.5
2,3,4,7,8-PeCDF	0.5
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDF	0.5
1,2,3,6,7,8-HxCDF	0.5
1,2,3,7,8,9-HxCDF	0.5
2,3,4,6,7,8-HxCDF	0.5
1,2,3,4,7,8-HxCDD	0.5
1,2,3,6,7,8-HxCDD	0.5
1,2,3,7,8,9-HxCDD	0.5
1,2,3,4,6,7,8-HpCDF	0.5
1,2,3,4,7,8,9-HpCDF	0.5
1,2,3,4,6,7,8-HpCDD	0.5
OCDF	1.0
OCDD	1.0

ATTACHMENT 3

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PCDDs AND PCDFs BY GC/MS - METHOD 8280A

TLI SOP No.	DHR187 Version: 1	Effective Date:	June 8, 1998
Author:	Wojciech Krol	Date Written:	February 6, 1998
Authorization:	Phil Albro (Management)	Date Authorized:	5/24/98

I. **SCOPE AND APPLICATION:** This method provides procedures for the analysis of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) from matrices including but not limited to soil, fly ash, and water, using procedures described in SW 846 Method 8280A.

II. **SAFETY CONSIDERATIONS:** The 2,3,7,8-TCDD isomer has been found to be acenegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in the 2,3,7,8 positions are known to have toxicities comparable to that of 2,3,7,8-TCDD. Extreme care must be exercised in all handling of extracts and standards in the application of this SOP. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDSs.

III. **EQUIPMENT:** The High-Resolution Gas Chromatograph/Low-Resolution Mass Spectrometer/Data System (GC/MS/DS) equipment utilized for this analysis includes the following:

A. Gas Chromatographs: Hewlett Packard 5890 or 5890 Series II (equipped for temperature programming and capillary columns)

B. Low Resolution Mass Spectrometers: VG 12-250 Quadrapole, VG 7070EQ, VG 70 SE ,VG Autospec

C. Data Systems: VG Analytical PDP11 with 11-250 software or VAX Alpha with Opus 3.2 software.

D. GC Injection Port - The GC injection port is designed for capillary columns. Two microliter (2 mL) injection volumes are used unless otherwise noted.

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PCDDs AND PCDFs BY GC/MS - METHOD 8280A	
TLI SOP No. DHR187 version: 1	Date written: February 6, 1996

E. Gas Chromatograph/Mass Spectrometer(GC/MS) Interface - The GC/MS interface components can withstand 350°C. The interface has been designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. The GC column is fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel®, or equivalent, ferrules are recommended.

F. Mass Spectrometer - The VG 7070EQ and VG 70SE units are high resolution mass spectrometers which are operated at low resolution (1000 - 3000) for this analysis. Each instrument is operated in the selected ion recording mode (SIR).

G. Data System - A dedicated data system is employed to control the rapid selected-ion monitoring (SIM) process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitation may be reported based upon computer generated peak areas or upon measured peak heights. The data system is set to acquire data as low as 10 ions in a single scan. Table 1. presents a listing of the ions which are typically monitored. The data system is set to switch to different sets of ions (descriptors) at specified times during an HRGC/LRMS acquisition. The data system provides hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It also acquires mass spectral peak profiles and provides hard copies of peak profiles to demonstrate the required resolving power. Measurements of noise on the base line are performed using the hard copies of individual ion chromatograms provided by the data system.

NOTE: The detector ADC zero setting must be set to allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power.

H. GC Columns -

1. In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one GC/MS analysis, the 60 m DB-5 fused silica capillary column is used.

2. The 2,3,7,8-TCDF isomer must be confirmed on a 30 m DB-225 fused silica capillary column when the TEF value is greater than or equal to 0.7 ppb in a ten gram solid sample or 7 ppt in a one liter water sample and the 2,3,7,8-TCDF isomer is reported as a concentration or an EMPC.

IV. STANDARDS:

A. Calibration Solutions (Table 2) - Five nonane solutions containing the unlabeled and labeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (0.1 ng/mL) and the highest values for the octachlorinated congeners (10.0 ng/mL).

Note: Only the mid-range calibration standard (CC3) contains the clean-up standard ($^{37}CL_4$-2,3,7,8-TCDD) and all of the unlabeled analytes.

B. Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at 0.5 ng/mL per compound. Twenty microliters (20 mL) of this solution is usually added to each sample extract before the GC/MS analysis.

C. GC Column Performance/Retention Window Check Solution (RTCHK)- This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. Table 3 lists the first and last eluting isomer for each homologue.

D. Acceptance Criteria for Newly Prepared Standards - All the components and concentrations of each calibration standard, recovery standard, internal standard, and matrix spike solution are verified prior to use for sample analyses. Testing consists of back to back analysis of the "test" solution (the newly prepared solution) and a "control" solution (a known good solution). Control solutions are isolated from the production standards in a protected location. Both the control and test solution are evaluated versus the current continuing calibration standard and versus each other. Each component of the test solution must be within 80-120% of the true concentration when calculated versus the control standard. The control standard must be within 80-120% of the true value when calculated versus the continuing calibration standard.

E. Storage Conditions - Standards are stored in 1/2 dram amber glass vials at room temperature.

V. SYSTEM PERFORMANCE CRITERIA

System performance criteria are presented below. It must be documented that all applicable system performance criteria specified in this Section are met before analysis for any sample is performed. Table 4 provides recommended GC conditions that can be used to satisfy the required criteria. During a typical 12-hour analysis sequence, the GC column performance and mass spectrometer resolving power checks must be performed at the beginning of the 12-hour period of operation. A routine calibration verification is required at the beginning of each 12-hour period during which samples are analyzed.

A. GC Column Performance

1. Inject the column performance check solution (Section IV. C.) and acquire selected-ion monitoring (SIM) data as described in Section III. E., III. F., and Table 4.

2. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers or between 2,3,7,8-TCDF and the peaks representing other TCDF isomers must be resolved with a valley of ≤ 25% (Fig. 1.), where:

   Valley Percent = (x/y) x 100

   x = height of valley measured between 2,3,7,8-TCDD or 2,3,7,8-TCDF and the closest TCDD or TCDF eluting isomers, and

   y = the peak height of 2,3,7,8-TCDD or 2,3,7,8-TCDF.

   In addition, the chromatographic peak separation between the 1,2,3,4,7,8-HxCDF and the 1,2,3,6,7,8-HxCDD in the CC3 solution must be resolved with a valley of ≤ 50%.

3. The acquisition time windows must be set to allow observation of the first and last eluting isomer of each congener. All first and last eluters of a homologous series should be labeled and identified on chromatograms.

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B. Mass Spectrometer Performance

The instrument is tuned with Perfluorokerosene (PFK) to achieve a static resolving power of 1000 - 3000 (10% valley).

VI. CALIBRATION PROCEDURES:

A. Initial Calibration (ICAL)- Initial calibration of the instrument is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any continuing calibration does not meet the required criteria listed in Section VI. B.

1. All five calibration solutions listed in Table 2 must be used for the initial calibration.

2. Tune the instrument with Perfluorokerosene (PFK) to achieve a static resolving power of 1000 - 3000 (10% valley).

3. Inject 2 mL of the GC column performance check solution (RTCHK)and acquire SIM mass spectral data as described earlier in Section III.F-G. Any further analysis must not be performed until it has been documented that the column performance criteria listed in section V. A. was met.

4. Using the same instrument conditions that produced acceptable results for the RTCHK (i.e. acquisition windows and TCDD resolution), analyze a 2 mL portion of each of the five calibration standards.

   a) The ratio of integrated ion current for the ions appearing in Table 5 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series).

   b) The ratio of integrated ion current for the ions belonging to the carbon-labeled internal, surrogate, alternate, and recovery standards must be within the control limits stipulated in Table 5.

      NOTE: Ion ratios for all 17 native analytes and 7 carbon-labeled internal and recovery standards must be within the specified control limits simultaneously in one run for each of the five calibration standard solutions. If the ion abundance ratios are outside the limits, corrective action must be taken and

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acceptable abundance ratios achieved before any samples may be analyzed.

c) For each SICP and for each GC signal representing the elution of a target analyte the signal-to-noise ratio (S/N) must be better than or equal to 10:1.

d) Referring to Table 6, calculate the 17 relative response factors (RRF) for unlabeled target analytes relative to their appropriate internal standards, according to the following formula:

$$RRF(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

where:

RRF(n) = Analyte RRF

A_x = sum of the integrated ion abundances of the quantitation ions (Table 3.) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 3.) for the labeled internal standards,

Q_{is} = quantity of the internal standard injected

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected.

The RRF(n) is a dimensionless quantity; the units used to express Q_{is} and Q_x must be the same.

e) Calculate the average analyte $\overline{RRF}$ and their respective percent relative standard deviations (%RSD) for the five calibration solutions. For %RSD and %D determination see equations below:

$$\overline{RRF}_{(n)} = \frac{1}{5}\sum_{j=1}^{5} RRF_{n(j)}$$

Where n represents a particular PCDD/PCDF (2,3,7,8 substituted congener), and j is the injection number (or calibration solution number).

f) The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

(1) For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF determined in Section V. A. 4. e).

(2) For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (PeCDF - two, HxCDF - four, HxCDD - three, HpCDF - two) the mean RRF used for those homologous series will be the *lowest* of the mean RRFs calculated for all individual 2,3,7,8-substituted congeners.

NOTE: HRGC/LRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are assumed to be the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

g) Referring to Table 7, calculate relative response factors (RRF) and average relative response factors (RRF) for internal, surrogate, and alternate standards relative to their appropriate recovery standards, according to the following formula:

$$RRF_m = \frac{A_s \times Q_{rs}}{Q_s \times A_{rs}}$$

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$$\overline{RRF}_m = 5\sum_{j=1}^{5} RRF_{(m)j}$$

where:

m = congener type,

j = injection number,

A_s = sum of the integrated ion abundances of the quantitation ions for a given standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard,

Q_{rs}, Q_s = quantities of, respectively, the recovery standard (rs) and a particular standard injected (pg),

$RRF_{(m)}$ = relative response factor of a particular standard relative to an appropriate recovery standard, as determined from one injection, and

$\overline{RRF}_{(m)}$ = calculated mean relative response factor of a particular labeled standard relative to an appropriate recovery standard, as determined from the five initial calibration injections.

5. Acceptance Criteria for Initial Calibration - The criteria listed below for acceptable calibration must be met before any analysis is performed.

   a) The percent relative standard deviations for the mean response factors from the 17 unlabeled standards and those for the labeled reference compounds must not exceed ± 15 percent. (Table 9)

   b) The S/N ratio for the GC signals present in every SICP (including the ones for the labeled standards) must be ³ 10.

c) The isotopic ratios (Table 5) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section VI. A. 5. a) is met, the analyte specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the continuing calibration criteria (Section VI. B.) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

B. Continuing Calibration Check (CONCAL) - Continuing calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and RTCHK.

1. Inject 2 mL of the CONCAL solution CC3 standard (Table 2), using the same HRGC/LRMS conditions as described in Section V., and used to determine and document an acceptable calibration as provided in Section VI. A. 5..

2. Acceptance Criteria for Continuing Calibration - The following criteria must be met before further analysis is performed.

a) The relative response factors obtained for the unlabeled analytes and labeled standards during the continuing calibration analysis must be within ± 30 percent of the mean values established during the initial calibration (Section VI. A. 4. e) and f)).

b) The ion-abundance ratios (Table 5) must be within the allowed control limits.

c) Signal to Noise ratios for unlabeled analytes must be greater than 2.5:1, and for labeled standards must be 10:1.

d) If an acceptable CONCAL cannot be achieved, the GC/MS system must be evaluated. If the instrument is determined fit to run, an acceptable initial calibration must be obtained before any sample may be analyzed.

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C. GC column performance check solution (RTCHK)

1. Must be analyzed prior to the analysis of a sample or standard (either initial or continuing)

2. Acceptance criteria for the initial RTCHK solution are:

   a) The resolution between 2,3,7,8-TCDD and the closest eluting TCDD isomer must produce a valley whose height above the baseline is no greater than 25% of the height of the 2,3,7,8-TCDD peak.

   b) The first and last eluting isomer for each class must be present in the associated retention time window.

D. Ending Sensitivity Check A Sensitivity Check must be performed before the end of a 12 hour period after successful mass resolution and RTCHK.

1. Inject 2 mL of the CONCAL solution CC1 standard (Table 2), using the same HRGC/HRMS conditions as described in Section V., and used to determine and document an acceptable calibration as provided in Section VI. A. 5..

2. Acceptance Criteria for Sensitivity Check - The following criteria must be met before further analysis is performed.

   a) The ion-abundance ratios (Table 5) must be within the allowed control limits.

   b) Signal to Noise ratios for unlabeled analytes must be greater than 2.5:1, and for labeled standards must be 10:1.

   c) The retention times of the labeled recovery standards must be within ten seconds of the labeled recovery standards in the continuing calibration at the start of the 12 hour clock.

   d) If an acceptable Sensitivity Check cannot be achieved, the samples run during the twelve hour clock must be evaluated. Any samples where the PCDDs/PCDFs are below the method detection limit or containing EMPCs must be reanalyzed

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VII. ANALYSIS

A. A valid analysis of column performance check, calibration and method or instrument blank must have been obtained prior to the analysis of any sample.

B. Remove the sample extract (blown to dryness) or blank from storage. Add 20 mL of recovery standard and mix thoroughly. Care must be taken to coat the walls of the vial several times to dissolve the sample material deposited on the walls during the concentration process.

NOTE: A final volume of 20 mL or more should be used whenever possible. A 10 mL final volume is difficult to handle, and injection of 2 mL out of 10 mL leaves little sample for confirmations and repeat injections, and for archiving.

C. Inject a 2 mL aliquot of the extract into the GC, operated under the GC conditions that have produced acceptable CONCAL and RTCHK results.

D. Acquire SIM data using the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run. The analyst may be required to monitor a PFK ion, not as a lock mass, but as a QC ion, in order to meet this requirement. It is recommended to examine the QC ion or lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements. Report any discrepancies in the case narrative

E. Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

1. Retention Times.

Note: In order to make a positive identification of the 2,3,7,8-substituted isomers, the labeled recovery standards must elute

within 10 seconds of the same standards within the continuing calibration analyzed at the beginning of the twelve hour clock.

a) For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 1.), must be within -1 to +3 seconds of the isotopically labeled standard.

b) For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract the retention time must fall within 0.005 retention time units of the relative retention times measured in the continuing calibration.

c) For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the RTCHK solution.

d) The ion current responses for both ions used in quantitation and the ion used for confirmation (e.g., for TCDDs: m/z 320, 322, and 259) must reach maximum simultaneously (± 2 seconds).

e) The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 332 and m/z 334) must reach maximum simultaneously (± 2 seconds).

2. Ion Abundance Ratios

The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned (Table 5).

3. Signal-to-Noise (S/N) Ratio

All ion current intensities must be ³ 2.5 times noise level for analytes and 10 times noise level for standards for positive

identification of a PCDD/PCDF compound or a group of coeluting isomers.

4. Polychlorinated Diphenyl Ether Interferences

In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N ³_2.5 is detected, at the same retention time (± 2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 3) channel or if the PCDPE signal is less than 10% of the PCDF signal. Should the PCDPE signal be greater than 10% of the PCDF signal, the peak is flagged 'X' and the concentration is reported as an EMPC, regardless of the ion abundance ratio.

F. Quantitation

1. For gas chromatographic peaks that have met specified criteria calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}(n)}$$

where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 1) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight or volume, in grams or liters, of the sample (solid or liquid), and

$\overline{RRF}(n)$= relative response factor for the analyte in the continuing calibration analyzed at the start of the 12 hour clock.

2. Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal Standard Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}(m)} \times 100$$

where:

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 3) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Table 3) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (Table 7),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}(m)$= relative response factor for the labeled internal standard relative to the appropriate (see Table 7) recovery standard in the continuing calibration analyzed at the start of the 12 hour clock.

3. The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

4. Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte

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required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, depending on the type of response produced during the analysis of a particular sample.

5. Samples giving a response for at least one quantitation ion that is less than 2.5 times the background level.

a) The area of the analyte is replaced by the noise level measured in a region of the chromatogram clear of genuine GC signals multiplied by an empirically determined factor. The detection limits represent the maximum possible concentration of a target analyte that could be present without being detected.

$$DL = \frac{2 \times 2.5 \times (F \times H) \times Q_{is}}{A_{is} \times \overline{RRF}_{(n)} \times W}$$

Where:

DL = estimated detection limit for a target analyte, expressed in ng or pg.

2.5 = minimum response required for a GC signal.

F = an empirical number that approximates the area to height ratio for a GC signal. (F= 3.7 for all dioxin/ furan analyses.)

H = height of the noise.

A_{is} = integrated current of the characteristic ions of the corresponding internal standard.

Q_{is} = amount of internal standard added to the sample before extraction.

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$RRF_{(n)}$ = mean analyte relative response factor from the CONCAL.

W = sample weight or volume.

6. Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

   a) When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet ion ratio requirements (Table 5) calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section VII. F. 1., except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

VIII. QUALITY CONTROL REQUIREMENTS

A. GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hour period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

B. Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks.

C. Routine sensitivity checks must be performed at the end of a 12-hour period during which samples are analyzed.

D. The target detection limits will be the following:

1. TDLs for waters (sample size 1 Liter):

   £ 10 ppt Tetra & PentaCDD & CDF
   £ 25 ppt Hexa & HeptaCDD & CDF
   £ 50 ppt OCDD & OCDF

2. TDLs for solids (sample size 10 grams):

   £ 1.0 ppb Tetra & PentaCDD & CDF
   £ 2.5 ppb Hexa & HeptaCDD & CDF
   £ 5.0 ppb OCDD & OCDF

E. Method Blank

1. Percent recoveries of all labeled standards should be between 25-150% Signal to noise for labeled standards must be ≥ 10:1.

2. Target detection limits must be met for each analyte.

3. No reportable analytes should be present in the Method Blank. Up to 3 analytes may be present at levels below 1/2 Target Detection Limit (TDL) as long as the compounds were not reported in the previous analysis.

4. For Method Blanks associated with high level samples, the analyte level in the blank must be < 5% of the quantity present in the samples.

F. LCS/ LCSD

1. Percent recoveries of all labeled standards should be between 25-150%. LCS/ LCSD with labeled standard recoveries below 25% are acceptable as long as signal to noise for affected standards is ≥ 10:1.

2. Percent recoveries of all analytes should be between 50-150

3. Relative percent difference between LCS and LCSD should be ≤ 50% for all analytes.

G. <u>Samples</u>

a) Internal standard recoveries in the sample are expected to be within 25 - 150 %. Samples having very complex matrices may not acheive the specified recoveries, but a S/N ³ 10:1 must be acheived.

b) The target detection limits (TDL) must be acheived, unless prohibited by a limited sample size or the need to dilute a high concentration sample.

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TABLE 1: ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HRGC/RMS FOR PCDDs AND PCDFs

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	242.9349	M+2-[COCl-]	$C_{11}H_4{}^{35}Cl_2{}^{37}Cl$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	258.9298	M+2-[COCl-]	$C_{11}H_4{}^{35}Cl_2{}^{37}ClO$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	331.9368	M	$13C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	276.8959	M+2-[COCl-]	$C_{11}H_3{}^{35}Cl_3{}^{37}Cl$	PeCDF
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	292.8908	M+2-[COCl-]	$C_{11}H_3{}^{35}Cl_3{}^{37}ClO$	PeCDD
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE

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TABLE 1: Continued

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
2	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8179	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	310.8570	M+2-[COCl-]	$C_{11}H_2{}^{35}Cl_5$	HxCDF
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	326.8520	M+2-[COCl-]	$C_{11}H_2{}^{35}Cl_4{}^{37}ClO$	HxCDD
	401.8558	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$13C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7769	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	344.8180	M+2-[COCl-]	$C_{11}H^{35}Cl_5{}^{37}Cl$	HpCDF
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	421.8190	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	360.8129	M+2-[COCl-]	$C_{11}H^{35}Cl_5{}^{37}ClO$	HpCDD
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE

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TABLE 1: Continued

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
3	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	378.7791	M+2-[COCl-]	$C_{11}{}^{35}Cl_6{}^{37}Cl$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7347	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	394.7740	M+2-[COCl-]	$C_{11}{}^{35}Cl_5{}^{37}Cl_2O$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE

a) The following nuclidic masses were used:

H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard

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TABLE 2 COMPOSITION OF INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (ng/mL) Sol. Number: 1	2	3	4	5
2,3,7,8-TCDD	0.1	0.25	0.5	1.0	2.0
2,3,7,8-TCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDD	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDF	0.1	0.25	0.5	1.0	2.0
2,3,4,7,8-PeCDF			0.5		
1,2,3,4,7,8-HxCDD			1.25		
1,2,3,6,7,8-HxCDD	0.25	0.625	1.25	2.5	5.0
1,2,3,7,8,9-HxCDD			1.25		
1,2,3,4,7,8-HxCDF			1.25		
1,2,3,6,7,8-HxCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,7,8,9-HxCDF			1.25		
2,3,4,6,7,8-HxCDF			1.25		
1,2,3,4,6,7,8-HpCDD	0.25	0.625	1.25	2.5	5.0
1,2,3,4,6,7,8-HpCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,7,8,9-HpCDF			1.25		
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-2,3,7,8-TCDF	0.5	0.5	0.5	0.5	0.5

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TABLE 2 Continued

Compound	Concentrations (pg/mL) Sol. Number: 1	2	3	4	5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-OCDD	1.0	1.0	1.0	1.0	1.0
Cleanup Standard					
$^{37}Cl_4$- 2,3,7,8-TCDD			0.25		
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5

PCDDs AND PCDFs BY GC/MS - METHOD 8280A	
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TABLE 3: GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION IV.C)

DB-5 COLUMN GC RETENTION TIME WINDOW DEFINING SOLUTION

CDD/ CDF	FIRST ELUTED	LAST ELUTED
TCDF	1,3,6,8	1,2,8,9
TCDD	1,3,6,8	1,2,8,9
PeCDF	1,3,4,6,8	1,2,3,8,9
PeCDD	1,2,4,7,9	1,2,3,8,9
HxCDF	1,2,3,4,6,8	1,2,3,4,8,9
HpCDF	1,2,3,4,6,7,8	1,2,3,4,7,8,9
HpCDD	1,2,3,4,6,7,9	1,2,3,4,6,7,8

DB-5 COLUMN TCDD SPECIFICITY TEST STANDARD

1,2,3,7 + 1,2,3,8 - TCDD
2,3,7,8 - TCDD
1,2,3,9 - TCDD

DB-225 COLUMN TCDF ISOMER SPECIFICTY TEST STANDARD

2,3,4,7 - TCDF
2,3,7,8 - TCDF
1,2,3,9 - TCDF

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TABLE 4: GAS CHROMATOGRAPHY CONDITIONS

Column type	DB-5	DB-225
Length (m)	60	30
i.d. (mm)	0.25	0.25
Film Thickness (um)	0.25	0.25
Carrier Gas	Helium	Helium
Carrier Gas Flow (mL/min)	1-2	1-2
Injection Mode	⇐ splitless ⇒	⇐ splitless ⇒
Valve Time (s)	60	60
Initial Temperature (C)	150	130
Injection Port Temperature	250	250
Program Temperature	See Note	

NOTE: The GC temperature is subject to change. Refer to work area guidelines for exact definitions of the current run conditions and descriptor name.

TABLE 5. ION-ABUNDANCE RATIO ACCEPTABLE RANGES FOR PCDDs AND PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

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TABLE 6. UNLABELED ANALYTES QUANTITATION RELATIONSHIPS

Homologue Group	Standard Used During Quantitation
TCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
PeCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
HxCDDs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
HpCDDs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
OCDD	$^{13}C_{12}$-OCDD
TCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
PeCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
HxCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDF	$^{13}C_{12}$-OCDD

TABLE 7: INTERNAL STANDARDS QUANTITATION RELATIONSHIPS

Internal Standard	Standard Used During Percent Recovery Determination
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

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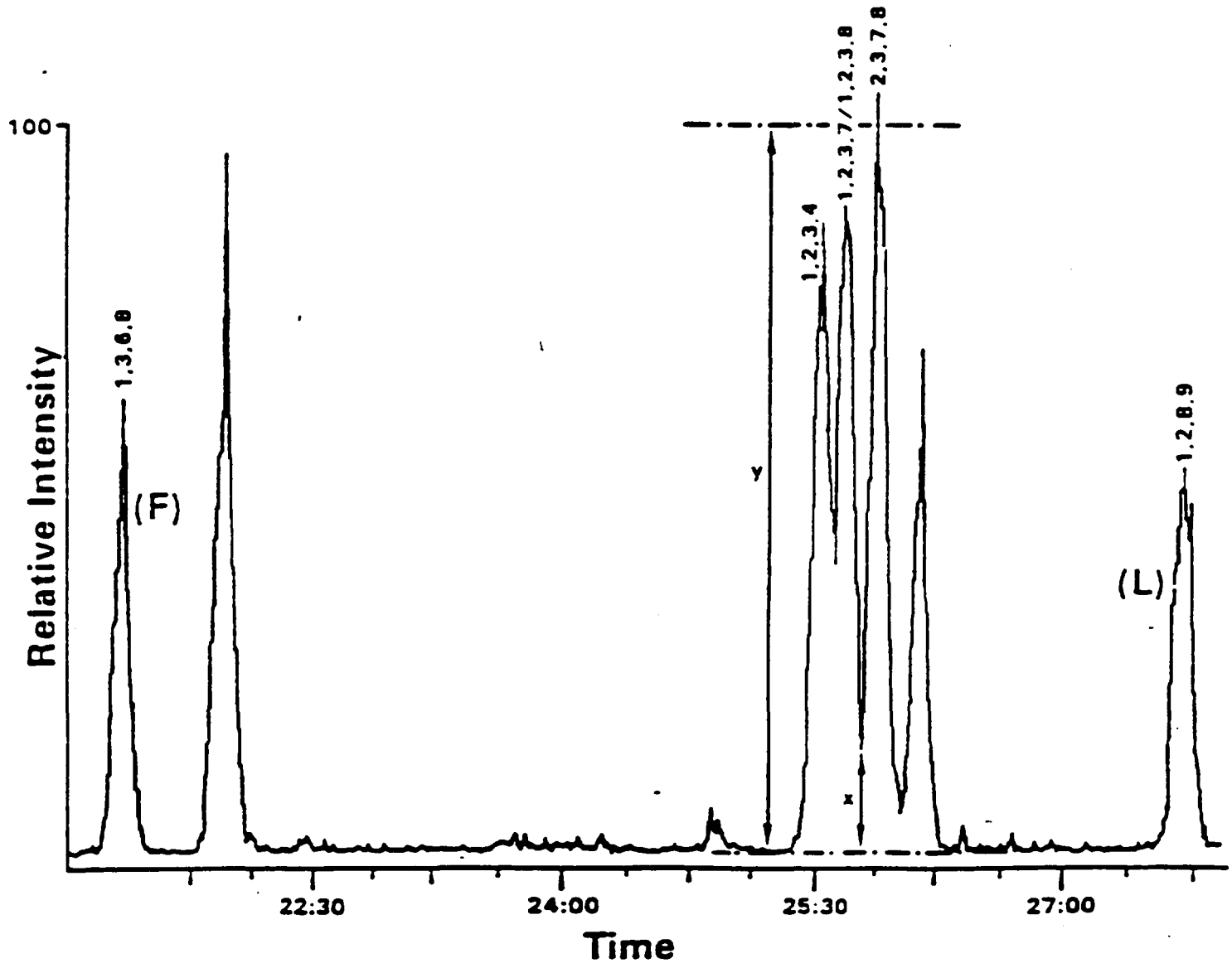
FIGURE 1. Valley between 2,3,7,8 - Tetra Dioxin and Furan Isomers and Other Closely Eluted Isomers.



Selected ion current profile for m/z 322 (TCDDs) produced by MS analysis of GC performance check solution on a 60 m x 0.32 mm DB-5 fused silica capillary column with 0.25 µm film thickness.

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CONFIDENTIAL and PROPRIETARY INFORMATION

PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290			
TLI SOP No. DHR182	Version: 6	Effective Date:	March 25, 1998
Author:	Wojciech Krol	Date Written:	February 9, 1998
Authorization: Management		Date Authorized:	2/16/98

I. **SCOPE AND APPLICATION:** This method provides procedures for the analysis of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) from extracts of samples prepared according to SW 846 Method 8290.

II. **SAFETY CONSIDERATIONS:** The 2,3,7,8-TCDD isomer has been found to be acenegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in the 2,3,7,8 positions are known to have toxicities comparable to that of 2,3,7,8-TCDD. Extreme care must be exercised in all handling of extracts and standards in the application of this SOP. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDSs.

III. **EQUIPMENT:** The High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (GC/MS/DS) equipment utilized for this analysis includes the following:

A. Gas Chromatographs: Hewlett Packard 5890 or 5890 Series II (equipped for temperature programming and capillary columns)

B. High Resolution Mass Spectrometers: VG 70 Series, VG 70-SE Series, VG Autospec.

C. Data Systems: VG Analytical PDP11 with 11-250 software or VAX Alpha with Opus 3.2 software.

D. GC Injection Port - The GC injection port is designed for capillary columns. Typically, 2 µL injection volumes are used unless otherwise noted.

E. Gas Chromatograph/Mass Spectrometer(GC/MS) Interface - The GC/MS interface components can withstand 350°C. The interface has been designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. The GC column is fitted directly into the mass spectrometer ion source without being

PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290	
TLI SOP No DHR182 Version: 6	Date Written: February 9, 1998

exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules are recommended.

F. Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

G. Data System - A dedicated data system is employed to control the rapid selected-ion monitoring (SIM) process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitation may be reported based upon computer generated peak areas or upon measured peak heights. The data system is set to acquire data as low as 10 ions in a single scan. Table 1. presents a listing of the ions which are typically monitored. The data system is set to switch to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system provides hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It also acquires mass spectral peak profiles and provides hard copies of peak profiles to demonstrate the required resolving power. Measurements of noise on the base line are performed using the hard copies of individual ion chromatograms provided by the data system.

NOTE: The detector ADC zero setting must be set to allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power.

H. GC Columns

1. In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, the 60 m DB-5 fused silica capillary column is used.

2. The 2,3,7,8-TCDF isomer must be confirmed on a 30 m DB-225 fused silica capillary column, when 2,3,7,8-TCDF is detected on the DB-5 column at a level greater than or equal to the target detection limit.

IV. STANDARDS:

A. Calibration Solutions Six nonane solutions containing 17 unlabeled PCDDs and PCDFs and 18 $^{13}C_{12}$ -labeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The analyte concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and

furan (0.5 pg/µL) and the highest values for the octachlorinated congeners (2000 pg/µL) (Table 2.).

B. Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. at a nominal concentration of 100 pg/µL per compound. A 20 µL of this solution is spiked into each sample extract before the HRGC/HRMS analysis.

C. GC Column Performance/Retention Window Check Solution (RTCHK)- This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of closely eluting TCDD and TCDF isomers for the purpose of documenting the chromatographic resolution (Table 3).

D. Acceptance Criteria for Newly Prepared Standards - All components and concentrations of each calibration standard, recovery standard, internal standard, and matrix spike solutions are verified prior to use for the analysis of samples. Testing consists of back to back analysis of the "test" solution (the newly prepared solution) and a "control" solution (a known good solution). Control solutions are isolated from the production standards in a protected location. Both the control and test solutions are evaluated versus the current continuing calibration standard and versus each other. Each component of the test solution must be within 80 - 120% of the true concentration when calculated versus the control standard. The control standard must be within 80 - 120% of the true value when calculated versus the continuing calibration standard.

E. Standards are stored in 1/2 dram amber glass vials at room temperature.

V. SYSTEM PERFORMANCE CRITERIA

System performance criteria are presented below. It must be documented that all applicable system performance criteria specified in this Section are met before analysis for any sample is performed. Table 4 provides recommended GC conditions that can be used to satisfy the required criteria. During a typical 12-hour analysis sequence, the GC column performance and mass spectrometer resolving power checks must be performed at the beginning of the 12-hour period of operation. A routine calibration verification is required at the beginning and end of each 12-hour period during which samples are analyzed. A method blank or HRGC/HRMS solvent blank is required between a calibration run and the first sample run.

A. GC Column Performance

1. Inject the column performance check solution (Section IV. C.) and acquire selected-ion monitoring (SIM) data as described in Section III. E., III. F., and Table 4.

2. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers or between 2,3,7,8-TCDF and the peaks representing other TCDF isomers must be resolved with a valley of $\leq$ 25% (Fig. 1.), where:

   Valley Percent = (x/y) x 100

   x = height of valley measured between 2,3,7,8-TCDD or 2,3,7,8-TCDF and the closest TCDD or TCDF eluting isomers, and

   y = the peak height of 2,3,7,8-TCDD or 2,3,7,8-TCDF.

3. The acquisition time windows must be set to allow observation of the first and last eluting isomer of each congener. All first and last eluters of a homologous series should be labeled and identified on chromatograms.

B. Mass Spectrometer Performance

1. The mass spectrometer must be operated in the electron ionization mode. It is recommended that the ionization potential be set to optimize sensitivity for the given column flow and source design. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analyses are performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation. It is recommended, however, that a check of the static resolution be made and documented by using the peak matching unit before and after each analysis. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

2. Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory. To that effect, use a lock-mass ion from the reference compound Perfluorokerosene (PFK) used for tuning the mass spectrometer and monitor and record the lock-mass ion channel during SIM acquisitions. The level of the reference compound (PFK) metered inside the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the selected lock-mass ion signal, regardless of the description number, does not exceed 10% of the full scale deflection for a given set of detector parameters. Under those

conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

3. Using PFK molecular leak and an appropriate ion within the scan window, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley).

   a) Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of the high-mass reference signal (m/z 416.9760) obtained during a peak matching experiment by using the low-mass PFK ion at m/z 330.9792 (or lower in mass) as a reference.

   b) The format of the peak profile representative allows manual determination of the peak resolution. The peak width (at 5% peak height) of the high-mass reference ion must not exceed 100 ppm (resolving power: 10,000). Peak width is determined by triangulation with no more than 10% allowance for sampling error. Instrumental ion transmission and resolution will be checked, adjusted and documented in case the resolution is below the minimum required 10,000 resolving power.

VI. CALIBRATION PROCEDURES:

A. Initial Calibration (ICAL)- Initial calibration of the instrument is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any continuing calibration does not meet the required criteria listed in Section VI. B..

1. All six calibration solutions listed in Table 2. must be used for the initial calibration.

2. Tune the instrument with PFK to achieve a static resolving power of at least 10,000 (10% valley) as described in section V. B..

3. Inject 2 µL of the GC column performance check solution and acquire SIM mass spectral data as described earlier in Section III. F. - G. Any further analysis must not be performed until it has been documented that the column performance criteria listed in section V. A. was met.

4. Using the same GC and MS conditions that produced acceptable results for the column performance check solution, analyze a 2 µL portion of each of the six calibration solutions with the following requirements.

a) The ratio of integrated ion current for the ions appearing in Table 5 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series).

b) The ratio of integrated ion current for the ions belonging to the carbon-labeled internal, surrogate, alternate, and recovery standards must be within the control limits stipulated in Table 5.

NOTE: Ion ratios for all 17 native analytes and 18 carbon-labeled internal and recovery standards must be within the specified control limits simultaneously in one run for each of the six (6) calibration standard solutions. If the ion abundance ratios are outside the limits, corrective action must be taken and acceptable abundance ratios achieved before any samples may be analyzed.

c) For each SICP and for each GC signal representing the elution of a target analyte the signal-to-noise ratio (S/N) must be better than or equal to 10:1.

d) Referring to Table 6., calculate the 17 relative response factors (RRF) for unlabeled target analytes relative to their appropriate internal standards, according to the following formula:

$$RRF(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

Where:

RRF(n)= Analyte RRF

A_x = sum of the integrated ion abundances of the quantitation ions (Table 1.) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standards,

Q_{is} = quantity of the internal standard injected (pg),

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RRF(n) is a dimensionless quantity; the units used to express Q_{is} and Q_x must be the same.

e) Calculate the average analyte $\overline{RRF}$ and their respective percent relative standard deviations (%RSD) for the six calibration solutions.

$$\overline{RRF}_{(n)} = \frac{1}{6}\sum_{j=1}^{6} RRF_{(n)j}$$

Where n represents a particular PCDD/PCDF (2,3,7,8 substituted congener), and j is the injection number (or calibration solution number).

f) The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

(1) For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF determined in Section V. A. 4. e).

NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}C_{12}$-OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}C_{12}$-OCDF with $[M]^+$ of OCDD). Therefore, the RRF for OCDF is calculated relative to $^{13}C_{12}$-OCDD.

(2) For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (PeCDF - two, HxCDF - four, HxCDD - three, HpCDF - two) the mean RRF used for those homologous series will be the average of the mean RRFs calculated for all individual 2,3,7,8-substituted congeners.

NOTE: HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are assumed to be the same as the

responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

g) Referring to Table 7. and 8. calculate relative response factors (RRF) and average relative response factors (RRF) for internal, surrogate, and alternate standards relative to their appropriate recovery standards, according to the following formula:

$$RRF_{(m)} = \frac{A_s \times Q_{rs}}{Q_s \times A_{rs}}$$

$$\overline{RRF}_{(m)} = \frac{1}{6}\sum_{j=1}^{6} RRF_{(m)j}$$

Where:

m	=	congener type,
j	=	injection number,
A_s	=	sum of the integrated ion abundances of the quantitation ions for a given standard,
A_{rs}	=	sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard,
Q_{rs}, Q_s	=	quantities of, respectively, the recovery standard (rs) and a particular standard injected (pg),
$RRF_{(m)}$	=	relative response factor of a particular standard relative to an appropriate recovery standard, as determined from one injection, and
$\overline{RRF}_{(m)}$	=	calculated mean relative response factor of a particular labeled standard relative to an appropriate recovery standard, as determined from the six initial calibration injections.

5. Acceptance Criteria for Initial Calibration - The criteria listed below for acceptable calibration must be met before any analysis is performed.

a) The percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the labeled reference compounds must not exceed ± 30%.

b) The S/N ratio for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.

c) The isotopic ratios (Table 5.) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section VI. A. 5. a) is met, the analyte specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the continuing calibration criteria (Section VI. B.) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

B. Continuing Calibration Check (CONCAL) - Continuing calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and QC resolution performance checks. A continuing calibration is also required at the end of a 12 hour shift.

1. Inject 2 µL of the CONCAL solution HRCC-3 standard (Table 2). By using the same HRGC/HRMS conditions as described in Section V., and used to determine and document an acceptable calibration as provided in Section VI. A. 5..

2. Acceptance Criteria for Continuing Calibration - The following criteria must be met before further analysis is performed.

a) The measured RRFs for the unlabeled standards obtained during the continuing calibration runs must be within ± 20 percent of the mean values established during the initial calibration (Section VI. A. 4. e) and f)).

b) The measured RRFs for the labeled standards obtained during the routine calibration must be within ± 30 percent of the mean values established during the initial calibration (Section VI. A. 4. g)).

c) The ion-abundance ratios (Table 5.) must be within the allowed control limits.

d) If either one of the criteria in Sections VI. B. 2. a) and b) is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire continuing calibration process must be reviewed.

e) If the continuing calibration at the end of a 12-hour period fails no more than 25% RPD for the unlabeled compounds and 35% RPD for the labeled reference compounds, use the mean RRFs from the two daily calibration runs to compute analyte concentrations, instead of the RRFs obtained from the initial calibration.

NOTE: If RRFs for up to two labeled standards fail by more than 35%, the calibration is considered acceptable, as long as corresponding unlabeled analytes meet criteria.

f) Continuing calibrations analyzed at the end of the 12 hour period which fail by more than 25% RPD for the unlabeled compounds and 35% RPD for the labeled reference compounds must be documented according to the non-conformance SOP. The analyst must assess the effect of failure on overall data quality. The assessment will include evaluation of any spiked samples included in the 12 hour "clock", presence of reportable levels of the affected analytes in the samples, and sample data obtained during the period between beginning and ending calibrations. All samples which contain reportable levels of a "failed" analyte will be reanalyzed unless a passing spiked sample has been analyzed between the sample and the ending calibration standard.

VII. ANALYSIS

A. A valid analysis of column performance check, calibration and method or instrument blank must have been obtained prior to the analysis of any sample.

B. Remove the sample extract (blown to dryness) or blank from storage. Add 20 µL of recovery standard and mix thoroughly. Care must be taken to coat the walls of the vial several times to dissolve the sample material deposited on the walls during the concentration process.

NOTE: A final volume of 20 µL or more should be used whenever possible. A 10 µL final volume is difficult to handle, and injection of 2 µL out of 10 µL leaves little sample for confirmations and repeat injections, and for archiving.

C. Inject a 2 µL aliquot of the extract into the GC, operated under the GC conditions that have produced acceptable CONCAL and RTCHK results.

D. Acquire SIM data using the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run. The analyst may be required to monitor a PFK ion, not as a lock mass, but as a QC ion, in order to meet this requirement. It is recommended to examine the QC ion or lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements. Report any discrepancies in the case narrative.

E. Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

1. Retention Times

   a) For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Table 1.), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 1.), must be within -1 to +3 seconds of the isotopically labeled standard.

   b) For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of eight congeners; Table 1.), the retention time must fall within 0.005 retention time units of the relative retention times measured in the continuing calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the 12 hour continuing calibration results.

   c) For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the RTCHK solution.

d) The ion current responses for both ions used in quantitation (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach maximum simultaneously (± 2 seconds).

e) The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously (± 2 seconds).

2. Ion Abundance Ratios

The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned (Table 5.).

3. Signal-to-Noise (S/N) Ratio

All ion current intensities must be ≥ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers.

4. Polychlorinated Diphenyl Ether Interferences

In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected, at the same retention time (± 2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 1.) channel or if the PCDPE signal is less than 10% of the PCDF signal.

F. Quantitation

1. For gas chromatographic peaks that have met specified criteria calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}_{(n)}}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 1.) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight or volume, in grams or liters, of the sample (solid or liquid), and

$\overline{RRF}_{(n)}$ = calculated mean relative response factor for the analyte.

2. Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal Standard Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}_{(m)}} \times 100$$

Where:

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (Table 7.),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}_{(m)}$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 7) recovery standard.

3. Calculate the percent recovery of seven surrogate and alternate standards using expression VII. F. 2..

NOTE: For the air samples (PUF, M-0023A) calculate percent recovery of five surrogate standards relative to their appropriate internal standards.

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4. If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compound exceeds the dynamic range of the instrument (i.e., saturation in a mass channel) then solvent will be added to the extract to bring the signal level into the instrument's dynamic range. Any dilutions must be pre-approved by the client.

5. The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

6. Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, depending on the type of response produced during the analysis of a particular sample.

   a) Samples giving a response for at least one quantitation ion that is less than 2.5 times the background level.

      The area of the analyte is replaced by the noise level measured in a region of the chromatogram clear of genuine GC signals multiplied by an empirically determined factor. The detection limits represent the maximum possible concentration of a target analyte that could be present without being detected.

$$DL = \frac{2 \times 2.5 \times (F \times H) \times Q_{is}}{A_{is} \times \overline{RRF}_{(n)} \times W}$$

      Where:

      DL = estimated detection limit for a target analyte, expressed in ng or pg.

      2.5 = minimum signal/ noise required for a GC signal to be accepted.

      F = an empirical number that approximates the area to height ratio for a GC signal. (F= 3.7 for all dioxin/ furan analyses.)

H	=	height of the noise.
A_{is}	=	integrated current of the characteristic ions of the corresponding internal standard.
Q_{is}	=	amount of internal standard added to the sample before extraction.
$\overline{RRF_{(n)}}$	=	mean analyte relative response factor from the initial calibration.
W	=	sample weight or volume.
2	=	used to account for the two signals present for every analyte.

b) Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet ion ratio requirements (Table 5.) calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section VII. F. 1., except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

VIII. QUALITY CONTROL REQUIREMENTS

A. GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hour period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

B. Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks and at the end of a 12-hour period following the analysis of samples.

C. The target detection limits will be the following:

1. TDLs for waters (sample size - 1L):

≤ 10 ppq	TCDD & TCDF
≤ 50 ppq	Penta - HeptaCDD & CDF
≤ 100 ppq	OCDD & OCDF

2. TDLs for solids (sample size - 10g):

   ≤ 1 ppt TCDD & TCDF

   ≤ 5 ppt Penta - HeptaCDD & CDF

   ≤ 10 ppt OCDD & OCDF

3. For air (e.g., PUF, M-0023A) or Wipes (sample size - 1):

   ≤ 50 pg TCDD & TCDF

   ≤ 250 pg Penta - HeptaCDD & CDF

   ≤ 500 pg OCDD & OCDF

D. Method Blank

1. Percent recoveries of all labeled standards should be between 40 - 135%. Method blank with standard recoveries below 40% (but ≥ 25%) is acceptable as long as signal to noise for affected standards is ≥ 10:1.
2. Target detection limits must be met for each analyte. (VIII. C.)
3. No reportable analytes should be present in the Method Blank. Up to 3 analytes may be present at levels below 1/2 Target Detection Limit (TDL) as long as the compounds were not reported in the previous analysis.
4. For Method Blanks associated with high level samples, the analyte level in the blank must be < 5% of the quantity present in the samples.

E. LCS/ LCSD and MS/ MSD

1. Percent recoveries of all labeled standards should be between 40 - 135%. LCS/ LCSD or MS/ MSD with labeled standard recoveries below 40% (but ≥ 25%) are acceptable as long as signal to noise for affected standards is ≥ 10:1.
2. Percent recoveries of all analytes should be between 70 - 130%. For up to two analytes, recoveries may be as high as 145% or as low as 60%, as long as the associated relative percent differences (%RPDs) meet criteria.
3. Relative percent difference between LCS and LCSD or MS and MSD should be ≤ 20% for all analytes. For up to two analytes, %RPDs may be higher (up to 35%), as long as the associated percent recoveries meet criteria.

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F. Samples

1. Percent recoveries of all labeled standards should be between 40 - 135%. Samples with standard recoveries below 40% (but ≥ 25%) are acceptable as long as signal to noise for affected standards is ≥ 10:1. In the case of OCDD internal standards, the OCDF analyte must be below TDL also.

2. Specific detection limits must not exceed the target detection limits unless prohibited by a limited sample size or the need for dilution.

3. If the method blank contains reportable analytes but those analytes are not detected in the sample, the sample data may be reported.

4. Samples which fail acceptance criteria listed above (VIII. F. 1. and 2.) or associated with failing method blank or LCS/ LCSD (VIII. D. 1. - 4.; VIII. E. 1. - 3.) must be reextracted and reanalyzed. Exceptions may be made for sample matrices which require extreme additional cleanup procedures.

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TABLE 1: ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HRGC/HRMS FOR PCDDs AND PCDFs

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$13C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)

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TABLE 1 CONTINUED

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
3 Continued	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$13C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{13}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	430.9729	LOCK	C_8F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)

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TABLE 1 CONTINUED

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
4 Continued	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

a) The following nuclidic masses were used:

H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion Selected for Monitoring the Instrument Stability During the GC/MS Analysis

b) Descriptor 1 contains mono-, di- and trichlorinated dibenzodioxins and dibenzofurans that are not quantitated by Method 8290.

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TABLE 2: COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL) Sol. Number: 1	2	3	4	5	6
Unlabeled Analytes						
2,3,7,8-TCDD	0.5	1	10	50	100	200
2,3,7,8-TCDF	0.5	1	10	50	100	200
1,2,3,7,8-PeCDD	2.5	5	50	250	500	1000
1,2,3,7,8-PeCDF	2.5	5	50	250	500	1000
2,3,4,7,8-PeCDF	2.5	5	50	250	500	1000
1,2,3,4,7,8-HxCDD	2.5	5	50	250	500	1000
1,2,3,6,7,8-HxCDD	2.5	5	50	250	500	1000
1,2,3,7,8,9-HxCDD	2.5	5	50	250	500	1000
1,2,3,4,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,6,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,7,8,9-HxCDF	2.5	5	50	250	500	1000
2,3,4,6,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,4,6,7,8-HpCDD	2.5	5	50	250	500	1000
1,2,3,4,6,7,8-HpCDF	2.5	5	50	250	500	1000
1,2,3,4,7,8,9-HpCDF	2.5	5	50	250	500	1000
OCDD	5	10	100	500	1000	2000
OCDF	5	10	100	500	1000	2000
Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100

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TABLE 2 CONTINUED

Compound	Concentrations (pg/µL) Sol. Number: 1	2	3	4	5	6
Internal Standards Continued						
$^{13}C_{12}$-OCDD	200	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100
Surrogate Standards						
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	10	50	100	200
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100
Alternate Standard						
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100

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TABLE 3: GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION IV. C.)

DB-5 COLUMN GC RETENTION TIME WINDOW DEFINING SOLUTION

CDD/ CDF	FIRST ELUTED	LAST ELUTED
TCDF	1,3,6,8	1,2,8,9
TCDD	1,3,6,8	1,2,8,9
PeCDF	1,3,4,6,8	1,2,3,8,9
PeCDD	1,2,4,7,9	1,2,3,8,9
HxCDF	1,2,3,4,6,8	1,2,3,4,8,9
HxCDD	1,2,4,6,7,9	1,2,3,4,6,7
HpCDF	1,2,3,4,6,7,8	1,2,3,4,7,8,9
HpCDD	1,2,3,4,6,7,9	1,2,3,4,6,7,8

DB-5 COLUMN TCDD SPECIFICITY TEST STANDARD

1,2,3,7 + 1,2,3,8 - TCDD
2,3,7,8 - TCDD
1,2,3,9 - TCDD

DB-225 COLUMN TCDF ISOMER SPECIFICTY TEST STANDARD

2,3,4,7 - TCDF
2,3,7,8 - TCDF
1,2,3,9 - TCDF

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TABLE 4: GAS CHROMATOGRAPHY CONDITIONS

Column type	**DB-5**	**DB-225**
Length (m)	60	30
i.d. (mm)	0.25	0.25
Film Thickness (um)	0.25	0.25
Carrier Gas	Helium	Helium
Carrier Gas Flow (mL/min)	1-2	1-2
Injection Mode	⇐ splitless ⇒	
Valve Time (s)	60	60
Initial Temperature (°C)	150	130
Injection Port Temperature (°C)	250	250
Program Temperature	⇐ See Note ⇒	

Note. The GC temperature program is subject to change. Refer to work area guidelines for exact definitions of the current run conditions and descriptor name.

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TABLE 5. ION-ABUNDANCE RATIO ACCEPTABLE RANGES FOR PCDDs AND PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1 43
6a	M/M+2	0.51	0 43	0.59
7b	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

a) Used only for ^{13}C-HxCDF
b) Used only for ^{13}C-HpCDF

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TABLE 6. UNLABELED ANALYTES QUANTITATION RELATIONSHIPS

Analyte	Standard Used During Quantitation
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
Other TCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
Other PeCDDs	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Other HxCDDs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
Other HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD	$^{13}C_{12}$-OCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
Other TCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Other PeCDFs	$^{13}C_{12}$-1,2,3,7,8-PeCDF
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF

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TABLE 6 CONTINUED

Analyte	Standard Used During Quantitation
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
Other HxCDFs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
Other HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDF	$^{13}C_{12}$-OCDD

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TABLE 7: INTERNAL STANDARDS QUANTITATION RELATIONSHIPS

Internal Standard	Standard Used During Percent Recovery Determination
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

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TABLE 8: SURROGATE/ALTERNATE STANDARDS QUANTITATION RELATIONSHIPS

Surrogate/Alternate/Cleanup Standard	Standard Used During Percent Recovery Determination
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	13C_{12}-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

NOTE : For air samples (PUF and M-0023A) recoveries of surrogate standards are quantitated relative to their appropriate internal standards.

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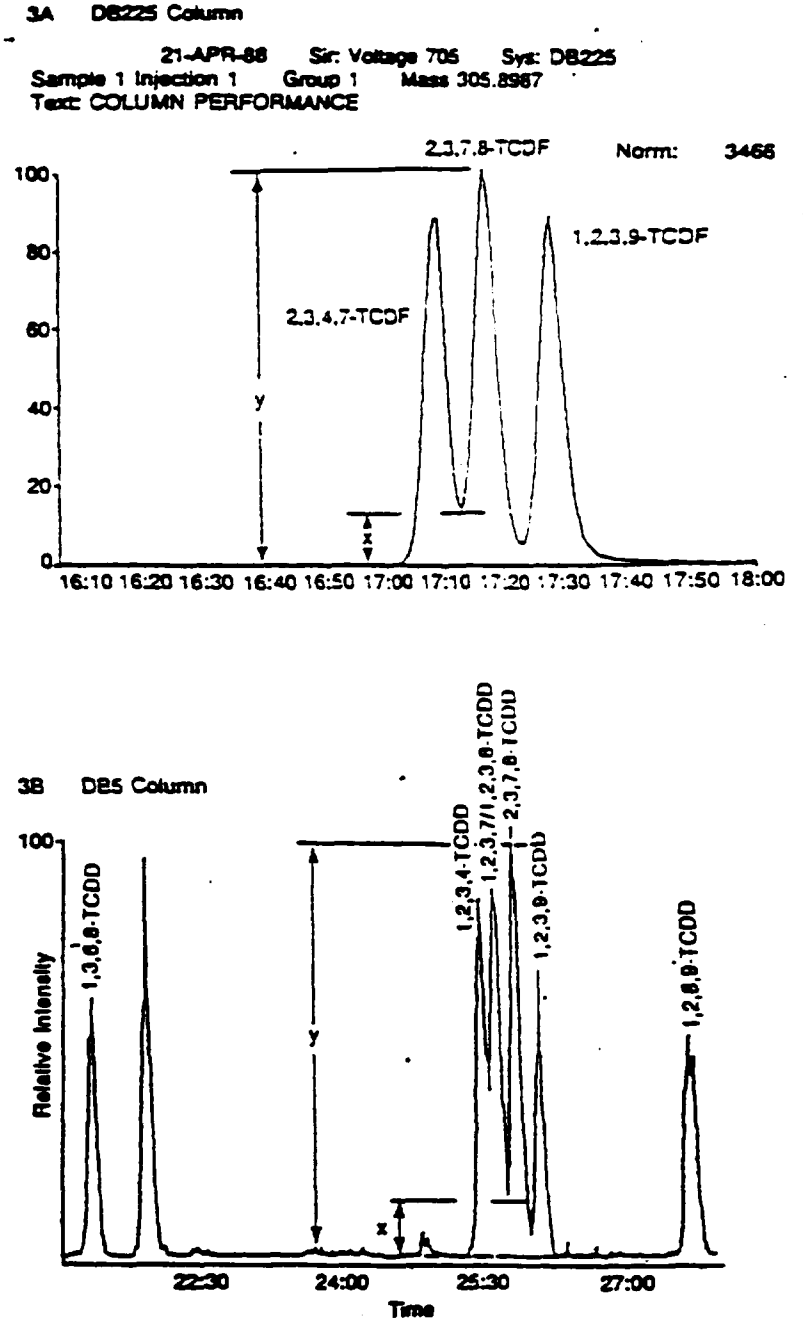

FIGURE 1. Valley between 2,3,7,8 - Tetra Dioxin and Furan Isomers and Other Closely Eluted Isomers.

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APPENDIX 1

Deviations from and improvements to US EPA Method 8290
POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/ HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/ HRMS)
as performed at Triangle Laboratories, Inc.

See Section	
• IV. A. and Table 2.	Triangle Laboratories uses 6 calibration points ranging from 0.5 pg/µL to 200 pg/µL for tetrachlorinated dioxin and furan. Concentrations of penta- through heptachlorinated analytes are 5 times higher than tetra congeners and octachlorinated analytes are 10 times higher (Compare with Table 5., Method 8290).
• IV. A.	Seven more labeled PCDDs/ PCDFs are used as surrogate and alternate standards to provide additional quality control information.
• IV. A.	The 1,2,3,6,7,8 - hexachlorodibenzofuran (HxCDF) is used as an internal standard instead of 1,2,3,4,7,8 - HxCDF. Triangle Laboratories uses 1,2,3,4,7,8 - HxCDF as a surrogate standard.
• IV. A.	Each carbon-labeled standard in the initial calibration solution has a concentration of 100 pg/µL except $^{13}C_{12}$ - OCDD, which is at 200 pg/µL. Concentrations of $^{13}C_{12}$ - labeled standards in sample fortification solutions are the same as in the initial calibration solution (See section 5.9., Method 8290).
• V.	The method blank does not need to be analyzed on each analysis clock that samples are analyzed. Once a valid analysis is provided for the method blank it may be replaced with HRGC/ HRMS solvent blank (See section 8.2., Method 8290).
• V. B. 3. a)	Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of m/z 416.9760 and 330.9792 (See section 8.2.2.3., Method 8290).
• VII. F. 6. a)	To calculate the sample specific Estimated Detection Limit, noise equivalent area is used instead of noise height (See section 7.9.5.1.1., Method 8290).
• VIII. D. - F. 1.	The Internal Standard recoveries in all QC samples and field samples are considered valid as long as the signal to noise ratio is greater than 10:1, the recovery is $\geq$ 25% and target detection limits for the analytes are met (See section 8.4., Method 8290).
• VIII. E. 2.	For up to two analytes in LCS/ LCSD and MS/ MSD, recoveries may be as high as 145% or as low as 60%, as long as the associated relative percent differences (%RPDs) meet criteria.

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APPENDIX 1 Continued

- VIII. E. 3. For up to two analytes in LCS/ LCSD and MS/ MSD, %RPDs may be higher (up to 35%), as long as the associated percent recoveries meet criteria.